Library

REGISTERED NO. M. 3121

# PROCEEDINGS

OF THE

# INDIAN ACADEMY OF SCIENCES

VOL. XIV] *SECTION A* [NO. 3

SEPTEMBER, 1941

*Price Rs. 2 or 3 Sh.* *Annual Subscription Rs. 18*

PRINTED AT THE BANGALORE PRESS, BANGALORE CITY, BY G. SRINIVASA RAO, SUPERINTENDENT, AND PUBLISHED BY THE INDIAN ACADEMY OF SCIENCES, BANGALORE.

# CONICAL REFRACTION IN NAPHTHALENE CRYSTALS*

By Sir C. V. Raman, V. S. Rajagopalan
and
T. M. K. Nedungadi
*(From the Department of Physics, Indian Institute of Science, Bangalore)*

Received August 22, 1941

## 1. *Introduction*

The phenomena of internal and external conical refraction in biaxial crystals predicted by Sir William Hamilton and observed by Humphrey Lloyd are amongst the most beautiful and striking effects arising in crystal optics. Following Lloyd's original experiments, these phenomena are usually exhibited with aragonite, a polished plate of this crystal suitably mounted between apertures and a viewing lens being employed for the purpose. The angles of internal and external conical refraction in aragonite are however small, ($\chi = 1° 52'$ and $\psi = 1° 42'$ respectively), and the use of other crystals, *e.g.*, tartaric acid with $\chi = 3° 54'$ and $\psi = 3° 58'$, and of sulphur for which $\chi = 7° 11'$ and $\psi = 7° 33'$ has therefore been sometimes suggested. It may be pointed out, however, that organic crystals of the aromatic class are specially suitable for the purpose. Naphthalene, in particular, exhibits birefringence in an exceptional degree, having as its principal indices 1·525, 1·722 and 1·945 respectively for $\lambda = 5461$ Å and its conical angles ($\chi = 13° 44'$ and $\psi = 13° 51'$) are enormously larger than in aragonite. Large single crystals of naphthalene can easily be prepared (Hilmi-Benel, 1940; Nedungadi, 1941), and the substance is thus well suited for exhibiting the optical characters of biaxial crystals and especially conical refraction in a striking way.

It may be remarked that apart from the purely geometrical aspects of optical theory illustrated by the Hamilton-Lloyd experiments, certain physical aspects of the propagation of light in biaxial crystals arising in conical refraction are of great interest. One of these is the enormous concentration of energy which occurs along the axis of single-ray velocity within the crystal and along the axis of the cone of external refraction outside it (Raman, 1921; Raman and Tamma, 1922). The converse phenomenon associated with internal conical refraction has long been known and is referred to in

* A preliminary note on this subject appeared in *Nature* of the 1st March 1941.

the literature as the Poggendorff dark circle. This was explained by Voigt (1905) as due to the attenuation of the energy of the incident pencil which occurs in single-wave propagation within the crystal. Both of these phenomena are well shown by naphthalene and in such manner as to bring out clearly their theoretical significance.

Conical refraction is often studied by viewing an illuminated pin-hole in focus through the crystal plate with a microscope or magnifying lens. It is generally supposed that what is then seen is internal conical refraction. That this is not quite correct was long ago pointed out (Raman, *loc. cit.*), but the matter was not then adequately discussed. Since the illuminated pin-hole is usually held close to the crystal and is backed by an extended source of light, the beam of light entering it is not restricted to any particular direction, and the effect observed is not therefore ascribable to internal conical refraction. Neither would it be altogether correct to ascribe it to external conical refraction; for, though with the pin-hole close to the crystal, a cone of light is incident on its first surface, no aperture limits the exit of the light from the second surface as in the Lloyd experiment. The focussed image of an illuminated pin-hole as seen in the microscope through the plate of crystal is formed by the entire bundle of rays issuing from the pin-hole and passing through the crystal and is thus a phenomenon distinct from either internal or external conical refraction, though related to both. As will be shown in this paper, the form of this image is determined by the curvature properties of the wave-surface in the crystal in the vicinity of the conical points. It is specially worthy of remark that when the microscope is focussed on the second surface of the crystal and not on the illuminated pin-hole, we see in the field of view an illuminated picture of the two sheets of the wave-surface, the conical point where they meet appearing as an intensely luminous centre, and the circle of contact with the tangent plane appearing as a dark ring (Fig. 7 in Plate X).

### 2. *Preparation of the Specimen*

A clear block of naphthalene can be grown by slow crystallization from a melt. Pure naphthalene redistilled several times is collected in a pyrex glass tube of about half-an-inch diameter, with its lower end drawn out tapering to a sharp point. The tube is suspended in a vertical furnace kept at a temperature from 10° to 15° C. above the melting point of naphthalene and gradually lowered out of it automatically by clockwork mechanism. Crystallisation starts at the tapering end of the tube and develops upwards. By proper control of the temperature of the furnace and of the rate of lowering of the tube, it is possible to get clear flawless blocks

of the single crystal of any desired length. It is removed from the container by momentarily heating the walls of the glass tube to a high temperature; the portion of the crystal in contact with it then melts and the crystal slips out.

As the crystal blocks prepared in this way do not possess any natural faces, advantage is taken of the fact that the axes of the optical and magnetic ellipsoids of the crystal roughly coincide to determine their orientation. The three magnetic axes of the crystal block may be determined by marking its preferred orientations in a strong magnetic field with different modes of suspension. The crystal block may be then cut with faces making any desired angle with these axes. To exhibit conical refraction, the naphthalene block should have its faces approximately normal to one of the primary optic axes, these being inclined at 42° to the acute bisectrix of the angle between them. For mounting the cut crystal, a flat surface is first ground and then quickly pressed on to a microscope cover slip kept at a temperature of about 40° above the melting point of naphthalene. The crystal face melts and wets the glass plate and immediately cools, thus resolidifying the melted layer as part of the single crystal in addition to making good optical contact with the glass. The second face of the plate is then treated in the same way. An alternative method of mounting is to grind the surfaces of the block smooth on a ground glass plate and then to polish them by rubbing quickly on a soft cloth stretched over a glass plate and moistened with a drop or two of xylene. Thin microscope cover clips may then be stuck on the faces with canada balsam. The mounted crystal may be conveniently fixed on a disc of aluminium having a central opening.

### *3. Method of Observation and Results*

The angles of conical refraction in naphthalene are so large that with a fairly thick piece, the phenomena can be seen directly with the simplest possible arrangements. For a critical study of the effects, however, and especially for securing satisfactory photographs, it is convenient to use a microscope with a revolving and centering stage and a Federov universal stage attachment on which the crystal plate is placed so that it can be tilted and set with its optic axis accurately parallel to the axis of the microscope. A low-power objective and a high-power ocular should be employed so that, for the same effective magnification, the largest working distance between the upper surface of the crystal and the objective of the microscope can be secured. For observing conical refraction under the microscope, a relatively thin plate of naphthalene (say two to three millimetres thick) is quite suitable. It is easy with these arrangements to photograph the cone

of external conical refraction and the cylinder of internal conical refraction outside the crystal in the manner of the Hamilton-Lloyd experiments. It is also possible to examine the relationships between these effects and the nature of the optical images obtained when a point-source of light is viewed through the crystal either in or out of focus.

Figs. 1–4 in Plate IX and Figs. 5–8 in Plate X reproduce a series of photographs obtained with the microscope camera attachment to illustrate the phenomena of conical refraction in naphthalene, the monochromatic green light $\lambda$ 5461 Å of the mercury arc being employed to avoid all disturbances due to chromatic aberration or dispersion. Fig. 1 shows the hollow cone of external conical refraction as seen above the crystal; to photograph this, both the upper and lower surfaces of the crystal are covered up except for small apertures situated at the ends of the axis of single-ray velocity, the lower aperture being illuminated by a convergent pencil of light. Fig. 2 shows the cylinder of internal conical refraction seen outside the crystal when a parallel beam of light is incident in the direction of the optic axis on the lower face of the crystal; to observe this, the lower face is covered by a screen with a small aperture and the second face is left uncovered. Figs. 3 and 4 in Plate IX and Figs. 5, 6, 7 and 8 in Plate X reproduce a consecutive series of photographs of a point source of light held close to the first surface and viewed through the crystal; Fig. 3 is the image seen in focus, while the other photographs in the series are ultra-focal images obtained when the microscope objective is gradually drawn away from the crystal. As already mentioned in the Introduction, Fig. 7 is the ultra-focal image of the point source of light obtained when the microscope is focussed on the second surface of the crystal. Fig. 8 is the ultra-focal image obtained when the microscope is still further drawn up. In obtaining this series of six pictures, the source of light was an extremely fine hole (1 $\mu$ in diameter) in an aluminium foil covering the lower surface on the crystal and illuminated by a convergent beam of light, while the second face of the crystal was left uncovered. The extreme sharpness of the circular ring seen in Fig. 3 is particularly significant. *It is noteworthy also that the so-called Poggendorff dark circle does not appear in the focal image of the point source and develops only in the ultra-focal images.* The extremely bright point seen at the centre in Fig. 7 (as also in Fig. 8 and very feebly in Fig. 2) is a noteworthy feature. This bright point in the ultra-focal image coincides with the end of the axis of single-ray velocity meeting the second surface of the crystal. This is shown by the fact that the second aperture for observing the cone of external conical refraction above the crystal (Fig. 1) has to be placed exactly at the same point so as to admit the light passing through the crystal. It is

evident from the series of pictures *that the axis of single-ray velocity and the conical point on the wave-surface are loci of intense concentration of energy within the crystal, while the circle of contact where the wave-surface touches the tangent plane is a locus of vanishingly small energy.*

### *4. Image Formation with a Biaxial Crystal*

It is well known (Stokes, 1877 and Walker, 1904) that the image of a point source of light seen through a crystalline plate exhibits astigmatism, being drawn out into a line perpendicular to the plane of principal curvature. For a biaxial crystal there are, in general, no fewer than four distinct positions of best focus determined by the orientation of the plate and by the principal radii of curvature of each of the two sheets of the wave-surface. In our present problem, we are concerned with the curvature of the wave-surface in the vicinity of the conical point and especially along the circle of contact with the tangent plane. At the conical point, one of the principal radii of curvature for each of the two sheets of the wave-surface vanishes, while the other two radii are

$$\rho_1 = b \text{ and } \rho_2 = (a^2 + c^2 - b^2)^{3/2}/ac.$$

At points along the circle of contact, one of the principal radii of curvature of each of the two sheets becomes infinite, while the other radius of curvature is

$$\rho = b \cdot (a^2 - r^2)\,(c^2 - r^2) \;/\; (a^2 - b^2)\,(c^2 - b^2),$$

$r$ being the length of the line joining the origin with any specified point on the circle of contact. At the two points where this circle cuts the circular and elliptic sections of the wave-surface respectively, the radii of curvature are

$$\rho_1' = b \text{ and } \rho_2' = b^3/a^2c^2.$$

In the case of naphthalene, $b^2$ and $ac$ are practically identical, as is readily seen from the numerical values of the principal refractive indices. As a consequence of this, also, the angles of internal and external conical refraction are practically identical. Hence, while one of the principal radii of curvature of the wave-surface is infinite along the circle of contact, the other radius of curvature is practically constant and equal to $b$ at all points on the circle and changes only slowly as we move away from the circle along the wave-surface either towards or away from the conical point. Accordingly, the astigmatism of the rays emerging from the plate results in an exceptionally simple form of the image, namely a sharply focussed circular ring having the same diameter as the circle in which the wave-surface makes contact with the second surface of the crystal.

As the microscope objective is drawn away from the crystal, the ultra-focal image necessarily alters continually. The rays reaching the upper surface of the crystal within the circle of contact bend inwards, while those outside the circle bend outwards, a gap appearing between them owing to the vanishing intensity at points along the circle. The rays that bend inwards appear to gain rapidly in intensity as they approach the centre of the field; the latter appears as a luminous point from which the rays appear to diverge, when the focal plane of the microscope coincides with the upper surface of the crystal.

The radiations from the point source entering the crystal may be regarded as an assembly of plane waves with coherent phase-relationships crossing each other at that point. Entering the crystal, their directions of travel are altered, and the resultant distribution of the energy stream within the crystal is determined by their superposition. Along the axis of single-ray velocity, the lines of energy flow of numerous sets of plane waves coincide and the density of the energy flow is therefore a maximum on this line. On the other hand, along the so-called cone of inner conical refraction, the energy-flow of a single set of plane-waves is divided up and the energy flow is therefore a minimum. Since the disturbance emerging from the crystal is determined by the superposition of the plane waves refracted out from it, the energy flow outside would be closely related to the special character of the energy flow within the crystal. Actually, the bright spot at the centre of the field may be traced for a great distance outside the crystal. The bright spot is, in effect, a spectral image of the original point source, its position varying with the wave-length of the light used (Raman and Tamma, *loc. cit.*).

## 5. *Summary*

The angles of internal and external conical refraction for naphthalene are exceptionally large (both about 13° 45′), and the substance is therefore exceptionally well suited for exhibiting these phenomena as well as for a critical study of the same. A series of eight photographs is reproduced with the paper and is discussed in detail. The following noteworthy effects are exhibited by the crystal. The so-called Poggendorff dark circle appears only in internal conical refraction and is an ultra-focal phenomenon, disappearing when the image of a point source of light seen in exact focus through the crystal plate, the image being then a single circular ring which is extremely sharp. In external conical refraction we have an effect converse to the Poggendorff phenomenon, *viz.*, a concentration of energy at the conical point of the wave-surface and therefore also along the axis of single-ray velocity. When the microscope is focussed on the second surface of the

FIG. 1

FIG. 2

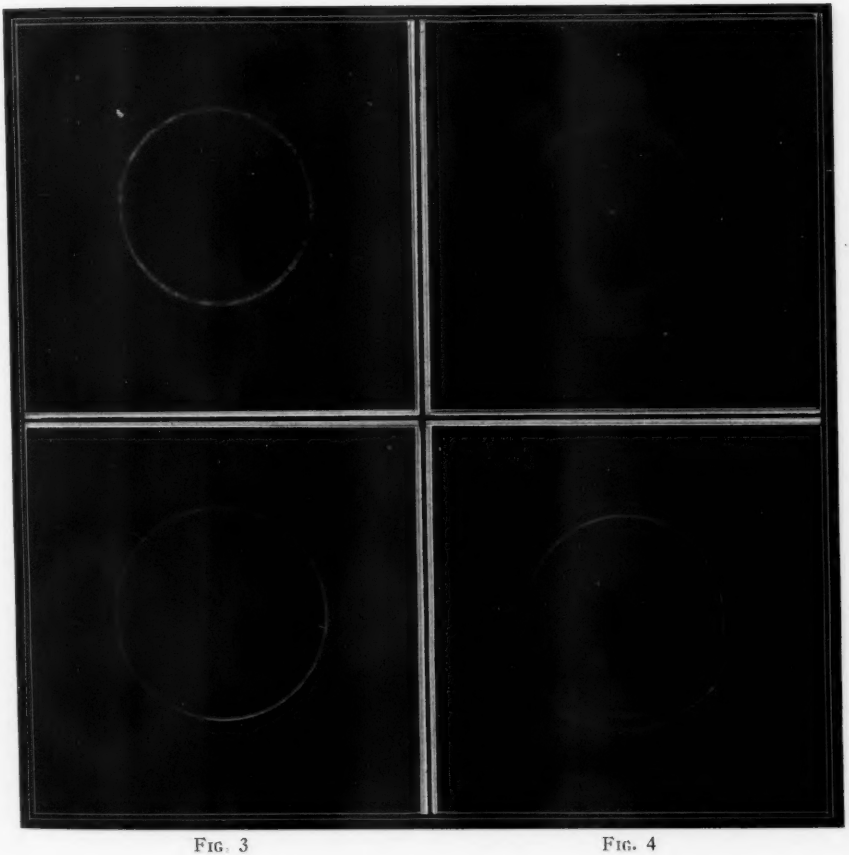


FIG. 3

FIG. 4

Illustrating Conical Refraction in a Naphthalene Crystal

FIG. 5

FIG. 6

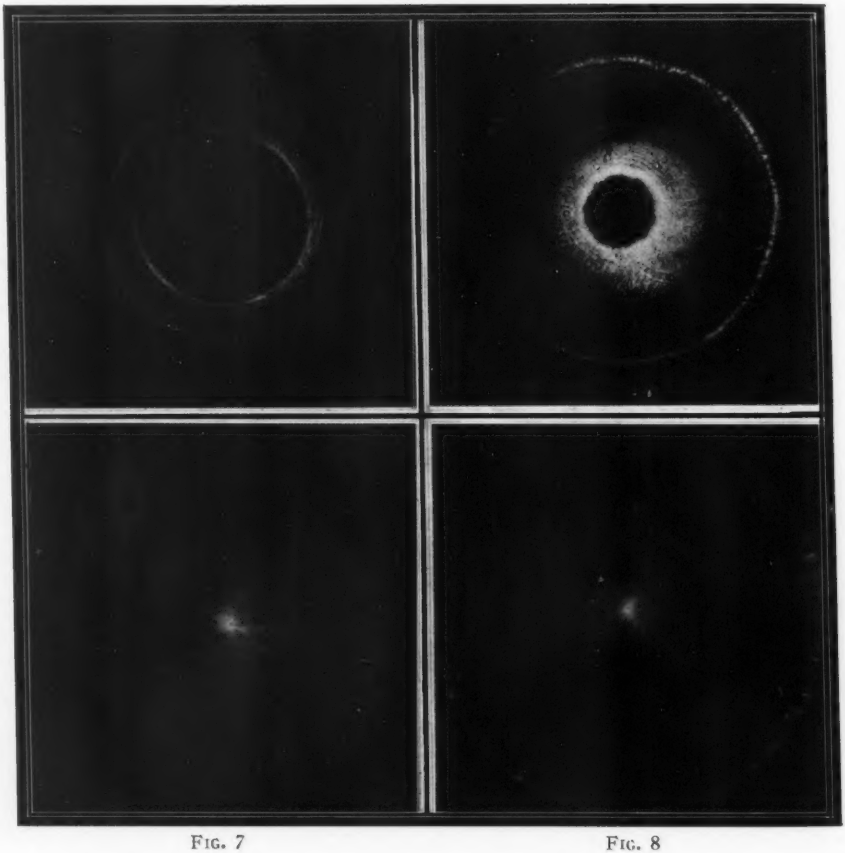


FIG. 7

FIG. 8

Illustrating Conical Refraction in a Naphthalene Crystal

crystal and not on the source of light, the field of view exhibits a picture of the wave-surface in two sheets, their intersection appearing as an intensely luminous point and the tangent plane to the surface as a dark ring.

## REFERENCES


| | | |
|---|---|---|
| Hilmi-Benel | .. | *Theses*, Bordeaux, 1940. |
| T. M. K. Nedungadi | .. | *Proc. Ind. Acad. Sci.*, 1941, **13**, 161. |
| C. V. Raman | .. | *Nature*, 1921, **107**, 747. |
| —— and V. S. Tamma | .. | *Phil. Mag.*, 1922, **43**, 510. |
| W. Voigt | .. | *Phys. Zeit.*, 1905, **6**, 673–818. |
| G. G. Stokes | .. | "*Scientific Papers*," Camb. Univ. Press, Vol. 5, p. 6. |
| J. Walker | .. | "*Analytical Theory of Light*," Camb. Univ. Press, Appx. III. |

# NEW METHODS IN THE STUDY OF LIGHT SCATTERING*

## Part I. Basic Ideas

By Sir C. V. Raman

*(From the Department of Physics, Indian Institute of Science, Bangalore)*

Received August 14, 1941

### *1. Introduction*

The scattering of light in material media may be considered from two distinct points of view: The first is that of the colloid chemist or biologist, the opalescence or Tyndall effect exhibited by whose media is related to the number, size and structure of the particles dispersed in them. The other point of view is that of the spectroscopist investigating the scattering of light in transparent substances and its relation to the molecular structure and the state of molecular aggregation. There is obviously a wide difference in the aims and methods of study adopted by these two groups of workers. This should not be permitted, however to obscure the essential similarities in the phenomena with which they are concerned. We have only one to mention some specific examples, *viz.*, optical glass, phenol-water mixtures, protein solutions and rubber dissolved in organic solvents, to realise the futility of setting out any rigid line of demarcation between "colloid" or turbid media, and "molecular" or transparent ones. Any such distinction must be conventional rather than logical. It will be realised, therefore, that the exchange of ideas and methods between the two fields of research should be of great importance for the progress of both.

### *2. The Reciprocity Relation*

An important step in the unification of colloid and molecular optics was taken by Dr. R. S. Krishnan (1934–1939) in his investigations at this Institute which established the "Reciprocity Relation" in the scattering of light and developed experimental methods based on its validity. This relation may be stated as follows: Consider *a parallel beam of plane-polarised light passing horizontally through an isotropic substance*, and let the scattered light be observed in a horizontal direction transverse to the incident beam. The intensity and state of polarisation of the transversely

* This paper reproduces the substance of a lecture delivered to the Indian Academy of Sciences at Bangalore on the 23rd September 1939.

scattered light would evidently depend on the azimuth of polarisation of the incident light. Krishnan's discovery was that, irrespective of the nature, size and shape of the particles of the scattering substance, $H_v = V_h$. These symbols represent respectively, the intensity of the horizontal vibration in the scattered light when the vibration in the incident light is vertical, and the intensity of the vertical vibration in the scattered light when that of the vibration in the incident beam is horizontal. A direct experimental proof of this result is furnished by the arrangement represented schematically in Fig. 1.

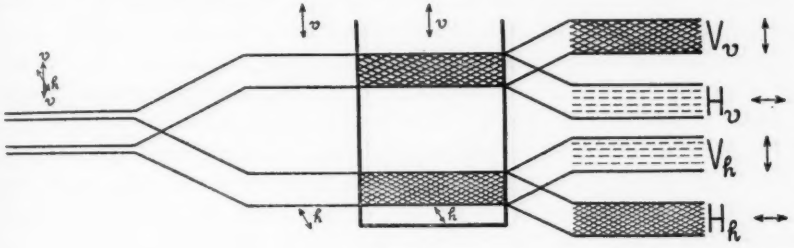



FIG. 1

Demonstration of Reciprocity Principle in Light Scattering

A beam of unpolarised light is divided by means of a double-image prism into two beams of *equal intensity* in which the electric vibrations are respectively vertical and horizontal. These beams enter the observation vessel containing the colloidal substance, and their tracks (which, in general, appear of unequal intensity) are viewed transversely through a double-image prism suitably held. We then see four tracks which may be designated as $V_v$, $H_v$, $V_h$ and $H_h$ respectively, the meaning of these symbols being clear from the figure. The equality of intensity of $H_v$ and $V_h$ in all cases is then directly evident to observation. The relative intensity of the four components $V_v$, $H_v$, $V_h$ and $H_h$ depends greatly on the size, shape and structure of the particles scattering light.

*If the particles are very small, spherical and isotropic,*

$$V_v \neq 0,\ H_v = V_h = H_h = 0. \tag{1}$$

*If the particles are not small but are spherical and isotropic,*

$$V_v \neq 0,\ H_v = V_h = 0,\ H_h \neq 0. \tag{2}$$

*If the particles are very small but are not spherical and isotropic,*

$$V_v \neq 0,\ H_v = V_h = H_h \neq 0. \tag{3}$$

*If the particles are neither small nor spherical and isotropic,*

$$V_v \neq 0,\ H_v = V_h \neq 0,\ H_h \neq 0. \tag{4}$$

The experimental facts stated in (1), (2), (3) and (4) are readily explained on the basis of the electromagnetic theory of light. The relations stated in (1) follows immediately from the fact that the particle in the conditions stated is equivalent to a simple Hertzian oscillator or electric dipole. The relationships stated in (2) follow immediately from the theory of scattering by spherical isotropic particles developed by Mie (1908). The radiations from the particle may be regarded as the result of the summation of a series of partial vibrations, *viz.*, a first electric, a first magnetic, a second electric, a second magnetic, a third electric, a third magnetic vibration and so on. The first and third electric vibrations, and the second and fourth magnetic vibrations in this sequence give a finite value for $V_v$ and zero values for $H_v$, $V_h$, and $H_h$, while the first and third magnetic vibrations and the second and fourth electric vibrations give a zero value for $V_v$, $H_v$, $V_h$ and a finite value for $H_h$. The superposition of these radiations gives the result stated in (2). The scattering of light by a very small ellipsoidal particle averaged for all orientations of the particle with respect to the field gives the result stated in (3). The relation $H_v = V_h$ is seen to be valid both in case (2) and in case (3). Hence, if the radiation from particles which are neither small nor spherical and isotropic is regarded as a superposition of the types of radiations considered in these two cases, the result $H_v = V_h$ must be valid also in the general case. Krishnan (1938) has given a different argument which also leads to the same result.

### 3. *The Krishnan Effect*

From the foregoing considerations, it follows that in the general case $V_h < H_h$. In other words, *if the incident beam is polarised with the electric vibration horizontal, the light scattered transversely would exhibit a partial polarisation in which the horizontal vibration is more intense than the vertical.* This is the Krishnan effect. The actual magnitude of the partial polarisation would be determined by the extent to which radiations of the types envisaged in (2) and (3) respectively enter, in other words by the relation between the size and the optical anisotropy of the particle. In the electromagnetic theory, the amplitude of the first electric radiation is proportional to the cube of the radius of the particle, while those of the first magnetic and the second electric radiations are proportional to its fifth power. Hence, the larger the size of the particle and the smaller its optical anisotropy, the greater would be the partial polarisation and the more readily, therefore, would it be detectable. *Vice versa*, the smaller the particle, and the larger its optical anisotropy, the more difficult of detection would be the partial polarisation of the transversely scattered light. The formulæ of the electromagnetic theory also indicate that the ratios of the amplitude of the higher

partial radiations relatively to the lower ones involve the wave-length of the light. This is evident since the ratios must evidently be dimensionless numbers, such as $a^2/\lambda^2$, $a^4/\lambda^4$, etc., where $a$ and $\lambda$ are respectively the radius of the particle and the wave-length of the radiation. Hence, for relatively small particles, the effect now under discussion must rapidly become more pronounced as the wave-length of the light is diminished.

### 4. *A Sensitive Method of Observation*

The partial polarisation of the scattered light referred to above may be readily demonstrated in a variety of cases. A Nicol which can be rotated polarises the light entering the colloid. The track of the beam passing through the observation vessel is viewed transversely through a double-image prism suitably held. It will then be noticed that as the Nicol is rotated and the direction of vibration in the incident beam turns round from the vertical to the horizontal position, the two images of the track seen alter in their relative intensity, the one which is stronger in the first case becomes the weaker in the second case. In other words, $V_v > H_v$ but $V_h < H_h$. The same effect can be shown in a more striking way by viewing the track through a Babinet compensator instead of through a double-image prism. As the polarising Nicol is rotated, the fringes seen in the compensator shift their position, indicating that the partial polarisation of the scattered light alters to a state in which the horizontal component instead of the vertical one is the more intense. As a means of detecting the partial polarisation, this technique is obviously more sensitive than observation through a double-image prism or a measurement of the depolarisation ratio which were the methods employed by Krishnan. A partial polarisation of only a few per cent. is detectable by the Babinet compensator. Hence, the range of the investigation is extended by its use to cases in which the difference of intensity between $V_h$ and $H_h$ is extremely small. Moreover, since the fringes in the Babinet compensator can be photographed, it becomes possible to extend the investigations into the ultra-violet region of the spectrum where, as already remarked, the magnitude of the partial polarisation is expected to become much larger.

The sequence of changes in the appearance of the field of the compensator as the polarising Nicol is rotated may be readily followed. It is evident that, since $V_v > H_v = V_h < H_h$, the fringes would be most marked when the vibrations in the incident light are vertical; their visibility would diminish and reach a minimum value at an oblique setting of the Nicol and increase again to a second maximum when the vibrations are horizontal. The setting of the Nicol at which the compensator fringes have the

minimum visibility would evidently depend on the ratio $V_v/H_h$. The fringes seen in the compensator appear on a background of uniform illumination due to the unpolarised or "anisotropic" part of the light scattering. The larger this is, the smaller would be the visibility of the fringes for all settings of the Nicol, and in particular at the setting in which the vibrations transmitted by it are horizontal. The sensitiveness of the method therefore diminishes with the increasing optical anisotropy of the particles arising from their non-spherical shape or structure.

### 5. *Ellipticity of the Scattered Light*

As was shown by Mie, we cannot expect to observe an elliptic polarisation in the light scattered by particles of any size, if the incident light is *unpolarised.* The position would, however, be altered, if the incident light is *plane polarised* in an arbitrary azimuth and the particles of the colloid are spherically symmetric and of uniform size. For, the incident vibration can then be resolved into vertical and horizontal components in a determinate phase relation, and the scattered radiations $V_v$ and $H_h$ arising respectively from these components would also be coherent, the phase relations between them being specifiable and the same for all the particles in the colloid. Unless, therefore, the relationship of phase is one of identity, the resulting radiation would be elliptically polarised. This would be indicated in the Babinet compensator by the position of the fringes which would correspond neither to a vertical nor a horizontal vibration but would be intermediate. In other words, when the Nicol polarising the incident beam is turned round from the vertical to the horizontal, the compensator fringes would shift continuously from one position to the other, remaining visible all the time. An effect of this kind should be easily noticeable when the particles in the medium are of the requisite type, *e.g.*, a cloud of water drops suspended in air or a dilute emulsion of one liquid in another. On the other hand, if the particles in the medium are of such a nature that there is no definite relation of phase between the components $V_v$ and $H_v$, then no elliptic polarisation should be detectable. In such a case, the compensator fringes would vanish at some particular setting of the Nicol, and re-appear in an altered position when the Nicol is rotated further in either direction.

### 6. *Applications of the Method*

The sequence of changes observed in the position and visibility of the compensator fringes as the polarising Nicol is turned round is thus closely connected with the structure of the medium scattering the light, and affords an insight into the mechanism of such scattering. In this connection, reference may be made to two very interesting papers by Dr. Hans Mueller

(1938) who has discussed the theory of the Krishnan effect from a standpoint which is very different from that set out above.

The technique described in the present paper would evidently be applicable to a great variety of cases and should be capable of yielding interesting results. In particular, the increased sensitiveness should enable the Krishnan effect to be looked for even in cases where it is undetectable with the methods previously employed, *e.g.*, colloids of the smallest particle size and even pure liquids. Preliminary work on these lines has been carried out with pure liquids and with liquid mixtures by Mr. T. A. S. Balakrishnan and on selected colloidal solutions and emulsions by Mr. Darbara Singh. Their results are described in a series of papers appearing in these *Proceedings* under the same title (Parts II, III, IV and V).

*Summary*

A method is described, based upon the use of a Nicol for polarising the incident beam in any desired azimuth and of a Babinet compensator for observing the transversely scattered light which enables the Krishnan effect to be very conveniently studied. The sensitiveness of the arrangement permits its use for the observation of the effect in cases where the methods previously employed are not delicate enough. It is pointed out that the magnitude of the effect would be enhanced by using ultra-violet radiation, the compensator fringes being recorded photographically. The same arrangement can also be employed for detecting and measuring the elliptic polarisation of the scattered light when the particles scattering the light are uniform and spherically symmetrical. The wide field of utility of the method in the study of light scattering is indicated.

REFERENCES

1. R. S. Krishnan .. *Proc. Ind. Acad. Sci.*, 1934, **1**, 211.
2. ———— .. *Ibid.*, 1935, **1**, 717.
3. ———— .. *Ibid.*, 1935, **1**, 782.
4. ———— .. *Ibid.*, 1935, **1**, 915.
5. ———— .. *Ibid.*, 1935, **2**, 221.
6. ———— .. *Ibid.*, 1936, **3**, 126.
7. ———— .. *Ibid.*, 1936, **3**, 211.
8. ———— .. *Ibid.*, 1936, **3**, 566.
9. ———— .. *Ibid.*, 1937, **5**, 94.
10. ———— .. *Ibid.*, 1937, **5**, 305.
11. ———— .. *Ibid.*, 1937, **5**, 407.
12. ———— .. *Ibid.*, 1937, **5**, 499.
13. ———— .. *Ibid.*, 1937, **5**, 551.

14. R. S. Krishnan .. *Proc. Ind. Acad. Sci.*, 1937, **5**, 577.
15. ———— .. *Ibid.*, 1938, **7**, 21.
16. ———— .. *Ibid.*, 1938, **7**, 91.
17. ———— .. *Ibid.*, 1938, **7**, 98.
18. ———— .. *Ibid.*, 1938, **8**, 442.
19. ———— .. *Ibid.*, 1939, **10**, 395.
20. G. Mie .. *Annalen der Physik*, 1908, **25**, 377.
21. Hans Mueller .. *Proc. Roy. Soc.* (A), 1938, **166**, 425.
22. ———— .. *Proc. Ind. Acad. Sci.*, 1938, **8**, 267.

# NEW METHODS IN THE STUDY OF LIGHT SCATTERING

## Part II. Pure Liquids

By T. A. S. Balakrishnan

*(From the Department of Physics, Indian Institute of Science, Bangalore)*

Received August 20, 1941

(Communicated by Prof. Sir C. V. Raman, Kt., F.R.S., N.L.)

### *1. Introduction*

It is well known that when a beam of unpolarised light traverses a column of dust-free liquid, the track of the beam observed in a transverse direction exhibits a partial polarisation, the extent of this depending on the liquid employed. The so-called depolarisation factor $\rho$ which is the ratio of the intensities of the vibration components respectively parallel and perpendicular to the plane of observation in the transversely scattered light depends on the liquid under study. It is relatively small for organic liquids of the aliphatic class, *e.g.*, carbon tetrachloride or ethyl ether, and much larger for liquids of the aromatic class, *e.g.*, benzene. If the beam of light is polarised before entry into the liquid, the depolarisation ratio is altered and then depends on the azimuth of polarisation of the incident light. According to R. S. Krishnan (1935) the following general equation is valid for all isotropic media

$$\rho_u = (1 + 1/\rho_h) \,/\, (1 + 1/\rho_v). \tag{1}$$

In this formula $\rho_u$, $\rho_v$, and $1/\rho_h$ represent the values of the depolarisation ratio, when the incident beam is respectively unpolarised and polarised with vibrations perpendicular and parallel to the plane of observation. According to present knowledge, in the case of pure liquids,

$$\rho_h = 1 \qquad \text{and therefore} \qquad \rho_u = 2\rho_v/(1 + \rho_v). \tag{2}$$

If the incident light be polarised with the vibrations making an angle $\theta$ with the vertical, the depolarisation ratio $\rho_\theta$ in the general case is, according to R. S. Krishnan (1939)

$$\rho_\theta = (1 + \tan^2\theta/\rho_h) \,/\, (\tan^2\theta + 1/\rho_v). \tag{3}$$

From formula (3), it follows that

$$\rho_v = \rho_{0°},\ \rho_u = \rho_{45°},\ \rho_h = 1/\rho_{90°}. \tag{4}$$

In the particular case when $\rho_h = 1$, formula (3) reduces to

$$\rho_\theta = \rho_v/(\rho_v \sin^2 \theta + \cos^2\theta) \qquad (5)$$

The question arises whether $\rho_h$ in the case of liquids is *exactly* equal to 1. Since the dimensions of molecules are very small compared with the wavelength, we may expect this to be the case provided that the scattering of light in a liquid may, as with gases, be assumed to be due to the individual molecules. But since a liquid is a dense aggregate of molecules, the latter assumption is questionable. Actually, the scattering of monochromatic light in a liquid is shown by spectroscopic research to be of several distinct kinds. Firstly, we have the Raman lines exhibiting relatively large frequency shifts. As the intensity of these lines relatively to the rest of the scattering is small in liquids, we shall not consider them further in the present connection. Secondly, we have the " wings " appearing in the spectrum on either side of the parent line in the incident radiation. This is due to hindered molecular rotation and is a depolarised radiation for which $\rho_h = 1$. Thirdly, we have the scattering by longitudinal sound waves appearing as a Brillouin doublet enclosing the parent line in the spectrum. Theory and experiment appear to agree in indicating that this radiation is completely polarised, *i.e.*, $H_v = V_h = H_h = 0$. Finally, we are left with the scattering of unmodified frequency, represented by an undisplaced line in the spectrum. This has been shown by B. D. Saxena (1938) and by Sunanda Bai (1941) to be polarised partially, but to varying extents for different liquids. The origin of this unmodified scattered radiation in liquids has not yet been fully elucidated, but it has been suggested that it may be connected with the quasi-static structure of the liquid, and that it is probably analogous to the unmodified scattered radiation observed with amorphous solids or glasses. It is conceivable that this scattering may be due, in part, to relative large clusters of molecules, in which case we may expect that $\rho_h < 1$. Whether this is actually so or not can only be decided by experiment.

That $\rho_h$ is practically unity in the case of pure liquids has long been known as a fact of observation. It is evident, therefore, that very sensitive methods would be required to exhibit any departure from this relation, the ordinary method of measuring depolarisation being inadequate for the purpose. In Part I of this series of papers, Sir C. V. Raman (1941) has suggested the use of a Babinet compensator or other sensitive polariscope for the detection of the effect. The purpose of the present investigation was to test out this idea, using a Babinet compensator to decide whether or not $\rho_h$ for pure liquids is unity. The results of a *preliminary* investigation with three pure liquids, namely, carbon tetrachloride, benzene and ethyl ether are recorded in the paper.

### 2. *Experimental Arrangements*

A pyrex glass cross of one-inch diameter with its four arms of length about 3 inches was taken. The fourth arm opposite the observation end was drawn out and bent up in the shape of a horn. The tip of the horn was connected to a glass flask which was filled with the liquid under investigation. The liquid was distilled over into the cross and then washed back into the flask about six or seven times so as to get it free of dust. After each distillation the liquid in the cross was tested with a strong beam of sunlight for any specks of dust. After the last distillation the cross was sealed off. It was blackened thoroughly on the outside except for three flat pyrex glass windows and then mounted in position. The observations were made in a dark cabin in the wall of which there was an aperture letting in a beam of sunlight reflected from a single-mirror Foucault heliostat. A Dallemeyer lens of focal length 12″ provided with a diaphragm to vary the aperture was fixed to the wall of the cabin in the path of the beam of sunlight and served to focus the incident illumination. Immediately after the lens, a glass cell with parallel plane end-pieces containing a solution of alum was placed to cut off the heat rays. Next to the cell was mounted a Nicol provided with a graduated circle which could rotate about the incident beam and thus cause the light to be polarised in any desired azimuth. The light after passing through the Nicol was focussed at the centre of the cross. To view the light transversely scattered by the liquid, the Babinet compensator was placed with its principal plane inclined at 45° to the plane of observation, in which position the compensator is most sensitive. The scattered light then passed through another Nicol oriented so as to transmit vibrations which had their electric vector horizontal. An eyepiece was used to make the visual observations. The eyepiece was removed and substituted by a camera with a lens having a maximum aperture of f/4·5 for taking photographs of the pattern of fringes formed in the field of vision. A series of filters ranging from a red filter to Wood's glass was used to study the phenomena at different wave-lengths. The photographs were taken on Selochrome or Ilford HP2 plates and developed with the Ilford Process plate developer.

There are several likely sources of error in the experiment. The first is the possibility of dust particles in the liquid giving a polarised scattering. This was eliminated by careful and repeated distillation. Secondly, the angle of convergence of the beam introduces some complications. This was avoided by making visual observations with continually reduced apertures. Thus when the apertures were reduced to as low a value as f/22, the liquids under investigation continued to exhibit the phenomena. The convergence

error for this aperture is very low and of the order of 0·03%. A third source of error lay in the diffuse scattering of light by the background. This was completely avoided by eliminating all extraneous light other than that passing through the cross, and the beam was kept so narrow that it did not impinge on the side of the cross anywhere in its track. The horn of the cross along with the thick coating of black everywhere on the outside combined to give a perfectly dark background over which the track of the incident light could be seen clearly. A series of diaphragms and screens completely cut out all extraneous light and there were similar diaphragms on the observation side of the cross in the path of the scattered light. The greatest care was exercised in seeing that only light scattered by the liquid at the centre of the cross was transmitted to the Babinet compensator and that no extraneous diffuse light had access to it.

### *3. Results*

The experiment was first conducted visually with the eyepiece mounted after the analysing Nicol in the path of the scattered light. When the incident light was polarised with its electric vector perpendicular to the plane of observation, the fringes in the Babinet's compensator appeared very brightly in the field of vision. The cross wire in the Babinet, consisting of a narrow fibre of silk stretched between the two quartz wedges, appeared on the central dark band. Since white light was used, coloured fringes were visible at the edges of the field. In the centre, however, there were three dark bands separated by white bright bands. Slowly turning the Nicol, the vibrations in the incident light were altered from the vertical to the horizontal and then further turned till they again became vertical. When this was done gradually, it was found that the fringes lost intensity, vanished completely and then reappeared again forming the same pattern as before. Midway when the vibrations were horizontal, there was a faint trace of illumination, and the question whether the fringes were present there or not could not be settled visually. The device of oscillating the Nicol rapidly about the position where the illumination was a minimum was then tried, and it was found that the fringes instead of disappearing completely showed up in a shifted position, the crosswire appearing on a bright band instead of on a dark band. Each time the Nicol was flicked about ten degrees on either side of the position at which the illumination in the field of the compensator was a minimum, the bands momentarily shifted their position and then came back to their original position. Thus the reversal of polarisation and the existence of fringes were both made clearly visible to the naked eye by this device. This reversal of polarisation was found to persist even at small apertures, up to about f/22. The eyepiece was now replaced by the camera and a series of

photographs taken for successive positions of the polarising Nicol, separated by one degree from the preceding position. Photographs of the fringe pattern formed at the Babinet compensator were taken for a range of ten degrees on either side of the horizontal position of the polarising Nicol. It was found that the fringe pattern shifted from one position to another within the space of a degree and that the fringes were very faint; they in fact almost disappeared at the position of transition. In the next setting of the Nicol separated by one degree from the position of transition, the photograph reveals the crosswire to be on a bright band. After this, the fringes continue to gain in intensity and become clearest when the vibrations in the incident light are horizontal. With further rotation, the fringe system loses intensity, till at the point of transition on the other side, they nearly vanish. In subsequent positions, the crosswire is seen on the dark band. If the rotation is carried on to make the vibrations in the incident light vertical, the fringe system is of maximum intensity.

The experiment was first conducted with carbon tetrachloride and five pictures are furnished in Fig. 1, Plate XI. The crosswire is on a black band for the first picture and the vibrations in the incident light are vertical. The reading on the graduated scale of the Nicol is 270°. The second position indicates the position of transition with the Nicol reading at 185°. Here the fringes have lost considerably in intensity and the crosswire is just visible over the black band. In the third picture the crosswire has shifted to a bright band and can be seen with two faint dark bands on either side. The Nicol reading for this position is 180°. The other two pictures show respectively the transition occurring at 175° and the fringe system with the vibrations in the polarised light vertical. The Nicol reading for the last picture is 90°.

The experiment was repeated with benzene. The reversal could not be observed visually. There was a certain quantity of general illumination in the field of vision and the fringes could not be seen when the vibrations in the incident light were horizontal. The field of view of the Babinet compensator and the analysing Nicol was photographed for successive positions of the Nicol. Among the five pictures furnished in Fig. 2, Plate XI the fringes are seen in two where the crosswire is on a dark band, but not in the other three. The corresponding readings for the settings of the polarising Nicol are given alongside.

The dependence of the polarisation of the scattering of light upon the wavelength was studied when the polarising Nicol was transmitting only horizontal vibrations. This was done by interposing suitable filters in the

path of the scattered light. Red, yellow, blue, violet and Wood's glass filters were used successively and a series of pictures with these filters are reproduced in Fig. 3, Plate XII. In all these cases the crosswire appears on a bright band and the reversal of polarisation can be seen more clearly with decreasing wavelength.

The experiment was repeated with ethyl ether which was also carefully distilled into a pyrex glass cross. Four pictures are reproduced in Fig. 4, Plate XII. They were also taken with the polarising Nicol oriented so as to transmit horizontal vibrations and with red, yellow, blue and violet filters. The reversal is exhibited by ether in a striking manner and the visibility of the fringes improves markedly when the violet filter is used for photographing the pattern of fringes.

In the case of benzene it was found that the fringes refused to register when the incident light had its vibrations horizontal even though the Wood's glass filter was used. All that could be obtained on the photographic plate was a certain quantity of general illumination and the dark crosswire. The failure to observe the effect with benzene is not surprising as benzene has a depolarisation ratio of 42% while those of carbon tetrachloride and ether are respectively 6% and 8·5%. The great intensity of the depolarised orientation scattering in the case of benzene would naturally overpower a feeble polarised scattering even if it were present.

The author desires to record his grateful thanks to Professor Sir C. V. Raman, F.R.S., for suggesting the problem and for valuable help during the course of the investigation. His thanks are also due to Dr. C. S. Venkateswaran for kind advice and assistance.

## *4. Summary*

Till now, it has been assumed that the light scattered in dust-free liquids is completely unpolarised when the incident light is polarised with its vibrations in the plane of observation. Using a Babinet compensator with an analysing Nicol oriented so as to transmit vibrations in the plane of observation, the author has established the presence of a feeble partial polarisation in the scattered light when the incident light is polarised as stated above. The presence of the feeble polarisation is shown by the appearance of fringes when the scattered light is viewed through the Babinet compensator. Photographs showing these fringes with carbon tetrachloride and with ether are reproduced. The fringes are, however, not observable in the case of benzene, being apparently masked by the much more intense unpolarised scattering

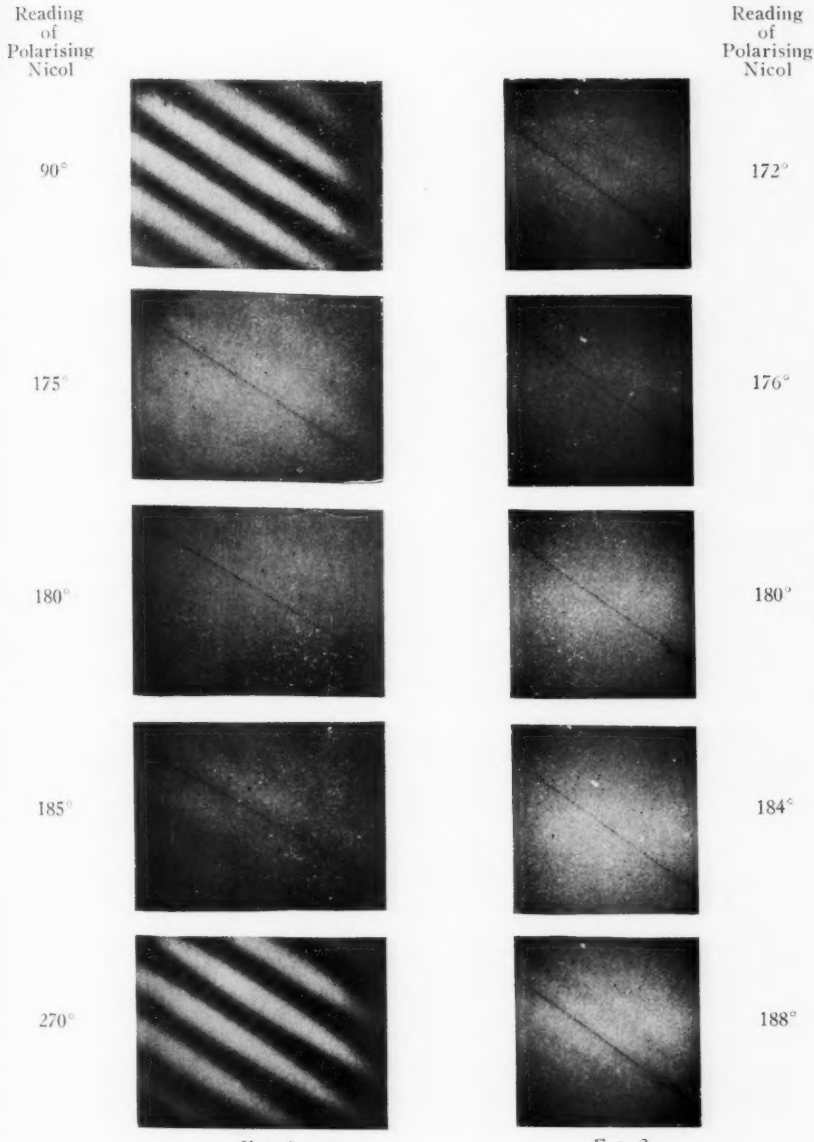



FIG. 1
Carbon tetrachloride

FIG. 2
Benzene

Light Scattering in Liquids observed through a Babinet Compensator

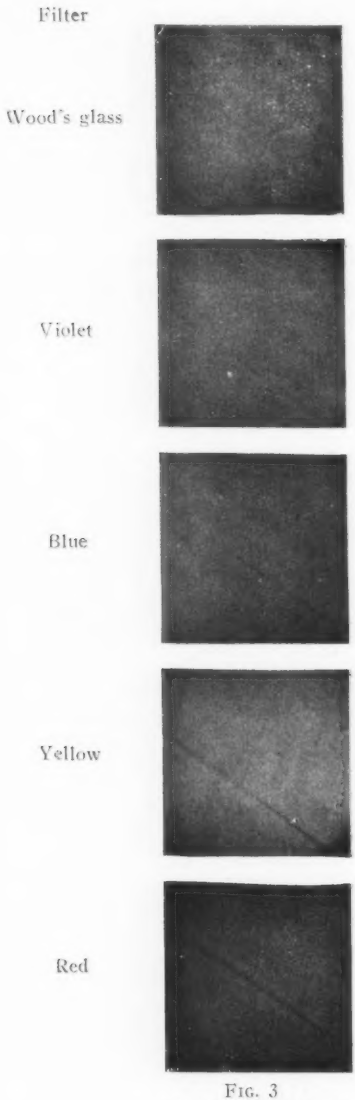



FIG. 3
Carbon tetrachloride

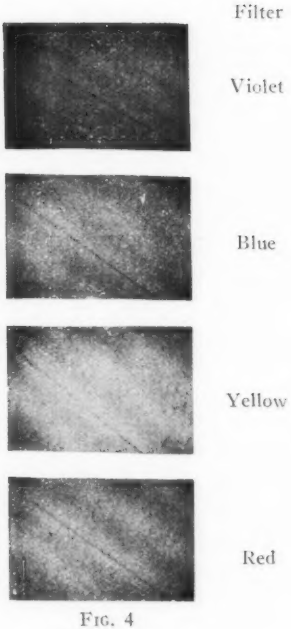



FIG. 4
Ethyl ether

Light Scattering in Liquids observed through a Babinet Compensator

present in the case of this liquid. The fringes noticed with carbon tetrachloride and ether become the more striking as the wave-length of the incident radiation is decreased.

REFERENCES


| | | |
|---|---|---|
| Krishnan, R. S. | .. | *Proc. Ind. Acad. Sci.* (A), 1935, **1**, 782. |
| ———— | .. | *Ibid.*, 1939, **10**, 395. |
| Raman, C. V. | .. | *Ibid.*, 1941, **14**. |
| Saxena, B. D. | .. | *Ibid.*, 1938, **8**, 460. |
| Sunanda Bai, K. | .. | *Ibid.*, 1941, **13**, 439. |

# STUDIES ON THE RAMAN EFFECT IN SINGLE CRYSTALS OF POTASSIUM NITRATE

By T. M. K. Nedungadi

*(From the Department of Physics, Indian Institute of Science, Bangalore)*

Received August 5, 1941

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

## *1. Introduction*

Potassium nitrate is well known to be chemically similar to sodium nitrate but crystallographically isomorphous with aragonite. Its structure bears the same relation to sodium nitrate as aragonite bears to calcite. Detailed studies have already been made on the Raman effect in sodium nitrate (Nedungadi, 1939) and calcite (Bhagavantam, 1940) with particular reference to the effect of crystal orientation on their spectra and these have yielded useful information regarding the dynamics of these crystals. By extending the study to potassium nitrate we can follow up the changes introduced in the spectrum due to change of symmetry and with the consequent change of environment of the $NO_3^-$ ion. Further, a study of the thermal effects on the spectrum of this crystal is interesting, because it undergoes a polymorphic transformation at 129° C. from orthorhombic to trigonal symmetry. We might expect to find important changes for the Raman lines, particularly for those due to lattice oscillations, following the transformation.

Research on the Raman effect in potassium nitrate has been mostly confined hitherto to the studies of the crystal powder, of the melt and of the aqueous solution with a view to find out the changes in the characteristic frequencies of the $NO_3^-$ ion due to change of state. Among the authors who studied the spectrum of the crystal previously, namely, Krishnamurti (1930), Menzies (1929), Bär (1929), Nisi (1931) and Anantakrishnan (1937), Nisi alone used a single crystal for his study. The frequency shifts observed by him are 31, 51, 84, 711, 1049 and 1344. Out of these the first three lines are attributed to the characteristic oscillations of the crystal lattice and the last three to the internal oscillations of the $NO_3^-$ ion. Line 1049 corresponds to $\nu_0$ the symmetrical breathing oscillation, while the lines 711 and 1344 are due to $\nu_3$ and $\nu_2$ the two doubly degenerate frequencies of the $NO_3^-$ ion. However, Anantakrishnan has observed that the line 1344 is really a doublet with frequency shifts 1341 and 1360. The frequency at 830 due to the oscillation of the N atom along the symmetry axis which is inactive in Raman effect for

the free ion has not been observed hitherto, though theory indicates that it should appear in the spectrum of this crystal. Further, the crystal aragonite yields six low frequency lattice oscillations (Rasetti, 1932) and it is natural to expect corresponding lines in potassium nitrate also. In these circumstances, a study of the dependence of the Raman lines on the temperature and also on the effect of crystal orientation has been made, and the results so far obtained are reported in the following pages.

## 2. *Experimental*

As potassium nitrate undergoes a polymorphic transformation between its melting point and the room temperature, it is impossible to grow single crystals from melts of the substance, as these while being cooled through the transformation temperature break up to form polycrystalline masses. The crystals used for the present study were, therefore, grown from solution. Great care had to be exercised in adjusting the saturation of the solution and maintaining the constancy of temperature of the crystallisation room in order to obtain fairly large clear single crystals. Crystals measuring $1 \cdot 5 \times 1 \times 0 \cdot 8$ cm. were obtained in the present case. The experimental arrangements used for the studies were practically the same as were described in some of the earlier papers of the author. However, the polaroid used hitherto for polarising the incident light was replaced by a large aperture (1 inch square) Ahren's nicol. The disadvantages of using a polaroid are threefold.—Firstly, its polarising power in the $\lambda$ 4358 region is not complete but only 90%. Secondly, it cuts off $\lambda$ 4046 to a large extent and hence observations on the Raman frequencies excited by this line cannot be made. Thirdly, the absorption of $\lambda$ 4358 itself is considerable. All these defects of the polaroid could be avoided by using a nicol, though this involves the sacrifice of part of the incident light intensity by the limited aperture of the nicol. For accurate quantitative results the incident light has to be strictly a parallel beam. This necessitates the using of a point source of light at the focus of a lens. However, practical considerations of the intensity of the incident beam for reasonable times of exposure, necessitate the use of a fairly large aperture condensing lens to focus the light from a vertical arc on to the crystal. This at present is an unavoidable evil. The semi-convergence angle thus introduced in the present study was about 10°.

## 3. *Raman Frequencies in the Spectrum*

Fig. 1 is a clear spectrum of the crystal recorded with the unpolarised light incident along the *b*-axis and the scattered light observed along the *c*-axis. The frequencies observed in a detailed analysis of this spectrogram are given in Table I.

TABLE I

| Raman lines | Excitation | Raman lines | Excitation | |
|---|---|---|---|---|
| 52 | *k, i, e* | 714 | *k, e* | *k*—λ 4046·5 Å |
| 82 | *k, i, e* | 1050 | *k, i, l, e* | *i*—λ 4077·8 „ |
| 100 | *k, e* | 1343 | *k, e* | *l*—λ 4347·5 „ |
| 126 | *k, e* | 1361 | *k, e* | *e*—λ 4358·3 „ |
| 143 | *e* | | | |

The following features of the spectrum may be specially noted: (1) Three new lines 100, 126 and 143 due to lattice oscillations have been recorded for the first time. (2) The two lattice lines 52 and 82 are very intense, the latter being much stronger than even the symmetrical oscillation 1050 of the $NO_3^-$ ion. (3) The line at 1350 due to the degenerate oscillation is a clearly resolved doublet consisting of sharp lines at 1343 and 1361. However, the other degenerate oscillation at 714 remains a sharp line. The aggregate intensity of the 714 line is roughly equal to the sum of the intensities of the separate components of the doublet at 1350. (4) No line due to the $\nu_1$ oscillation of the $NO_3^-$ ion is recorded at about 830 as in the case of aragonite. A lattice line at 31 with zero intensity reported by Nisi appears to be doubtful as it is not noticed in any of the strongly exposed plates of the present author in spite of the fact that three weak new lattice lines have been clearly recorded.

Bhagavantam (1941) has shown from group theoretical considerations that orthorhombic crystals of aragonite and $KNO_3$ should yield 18 Raman lines due to lattice oscillations. Six have been recorded by Rasetti for aragonite using the λ 2537 excitation of the mercury arc. The new lattice lines observed in $KNO_3$ are thus seen to be a necessary consequence of the orthorhombic symmetry of the crystal. That the line 82 in $KNO_3$ corresponds to the line 185 in $NaNO_3$ and is due to the tilting oscillations of the $NO_3^-$ ions in the lattice will be shown in a later section. The great intensity of the lattice lines 52 and 82, particularly of the latter, can be easily observed in the spectrogram. In the paper of the present author referred to earlier, it has been shown that the intensities of the symmetrical oscillation and of the tilting oscillation of the $NO_3^-$ ion are inversely proportional to their frequencies and that as a consequence, in the case of $NaNO_3$ where the corresponding lines are at 1065 and 185, the latter should be stronger of the two even when the crystal is oriented in a manner most favourable for recording the 1065 line strongly.

In the case of $KNO_3$ the tilting oscillation has a much lower frequency, nearly half that of $NaNO_3$, whereas the symmetrical oscillation of the $NO_3^-$ ion has practically the same value. Hence, it is but natural to expect that the line 82 should be stronger than the line 1050. The doubling of the degenerate line 1350 should be a consequence of the $NO_3^-$ ion which has a threefold axis of symmetry going into a less symmetrical orthorhombic lattice which has no axis of symmetry of an order higher than two. Further, it is to be expected that the line 714 would also split up into a doublet as the modes of oscillation of the $NO_3^-$ ion giving rise to both these lines are confined to the plane of the ion and are fundamentally similar. That this line actually consists of two separate components is shown by polarisation studies. The interesting observations on these and on the relative behaviour of the components of the doublet at 1350 with varying orientation of the crystal even when the incident light is unpolarised will be described in a later section.

The $\nu_1$ frequency of the $NO_3^-$ ion corresponds to a vibration of the N atom perpendicular to the plane of the ion. As it involves only a change in the electric moment of the ion and not a change in its polarisability this oscillation is inactive in Raman effect but active in infra-red. When the ion goes into the orthorhombic crystal lattice, the change in the selection rules enables the appearance of this oscillation in Raman effect theoretically. Special attempts were made by the present author to record this line in $KNO_3$ but without success. Spectra in which even the degenerate lines are intense do not show any indication of this line. It appears, therefore, that the polarisability changes accompanying this oscillation caused by the influence of the neighbours on any $NO_3^-$ ion are quite inappreciable. The corresponding line at 852 reported by Rasetti in aragonite is also apparently very feeble as it cannot be detected in the spectrum reproduced by him in his paper in spite of the fact that all the other lines he reports are easily visible in the same.

### 4. *Effect of Temperature on the Raman Spectrum*

Spectra of a single crystal of potassium nitrate were taken at 25°, 120°, 170° and 290° C. For a comparison of the effects produced by change of state, a spectrum of the substance in the molten state (m.p. 334° C.) was also recorded. With a uniform temperature field inside the heater the crystal could be heated gradually beyond the transformation temperature (129° C.) without fracture. Nevertheless, in the process of cooling it invariably cracked up below the transition temperature into micro-crystals. The frequency shifts of the crystal measured at the room temperature, at 290° C., as also those in the melt are recorded in Table II. Figs. 2 *a* and 2 *b* are the spectra taken with a Hartmann diaphragm at temperatures 25° and 120° C. respectively.

TABLE II

| | Lattice Oscillations | | | | $\nu_3$ | $\nu_0$ | $\nu_2$ | |
|---|---|---|---|---|---|---|---|---|
| Crystal at 25° C. .. | 52 | 82 | 100 | 126 | 714 | 1050 | 1343 | 1361 |
| Crystal at 290° C. .. | .. | .. | .. | .. | 710 | 1047 | 1330 to 1365 | |
| Molten 350° C. .. | Wing extending up to 95 cm.$^{-1}$ | | | | 710 | 1045 | 1265 to 1420 | |

A significant observation made in the present study is that the two lattice oscillations with frequency shifts 100 and 126 and presumably also the one at 143 broaden out and practically vanish at 120° C. as may be seen in Figs. 2 *a* and 2 *b*. It is clear that these lattice lines which are absent in the case of sodium nitrate are a consequence of the lower symmetry of potassium nitrate crystal. Hence, it is natural to expect that when the $NO_3^-$ ion finds itself in the field of trigonal symmetry, these new lines should disappear. The observation is analogous to that made by the author in the case of $\alpha$-quartz in which a particular oscillation of frequency shift 207 vanishes at the temperature of transition to $\beta$-quartz (Nedungadi, 1940). This observation in potassium nitrate also confirms the idea that a polymorphic transition in crystals involving an increase of its symmetry is characterised by the disappearance of certain oscillations of the lattice.

There is general similarity, as might be expected, between the variation with temperature of the Raman lines of sodium nitrate and potassium nitrate. The behaviour of the lattice lines 52 and 82 is generally similar to that of 98 and 185 respectively of sodium nitrate. Nevertheless, the line 82 broadens much faster than the corresponding line of sodium nitrate. Even at 170° C. the line is a very broad band. Greater details regarding the behaviour of these lines could not be made out due to the halation round the Rayleigh line developed at high temperatures.

As regards the internal oscillations, the rate of broadening of the lines with temperature is very slow. However, even at 120°C. the two lines 1343 and 1361 constituting the doublet have broadened out and consequently appear weaker though the doublet structure is still discernible. On the other hand at 170° C. (which is above the transition temperature) these two component lines have broadened out so much as to merge into one another and appear as one band. At 290° C. this line broadens further and extends over 35 cm.$^{-1}$ while the line 714 still remains comparatively sharp. The frequency shifts for these internal oscillations remain appreciably unaltered up to 290° C.

In the melt the lines due to internal oscillations are much broader than even in the crystal at 290° C. but the change in the frequencies due to change of state is not so conspicuous as in the case of sodium nitrate. The degenerate oscillation at 1350 is very broad in the melt and extends over 150 cm.$^{-1}$ It is noteworthy that the wing accompanying the Rayleigh line extends much less in $KNO_3$ compared to $NaNO_3$, though the distribution of intensity in the wing is similar in both substances. Some of these characteristics of the molten substance have been clearly recorded previously by Moses (1939).

### 5. *Effect of Crystal Orientation on the Raman Spectrum*

As usual in studies on the orientation effect on the spectrum of the light scattered by crystals in a transverse direction, we designate the direction of the incident beam by OX and of observation of the scattered light by OY, OZ being perpendicular to both. For a biaxial crystal with the principal optical directions* $\alpha$, $\beta$ and $\gamma$, it can be easily shown that we can obtain 54 different spectra for different orientations of the crystal with respect to the directions of incidence and observation and for different states of vibration of the incident and scattered light. This includes 6 spectrograms when the incident light is unpolarised and the scattered light is not analysed, 12 when the incident light is unpolarised and the scattered is analysed, 12 when the incident light is polarised and the scattered light is not analysed and 24 when the incident light is polarised and the scattered light is also analysed. It is obvious that the last 24 are the most important as they comprise the results of the rest also. It should be pointed out here that the potassium nitrate crystal, though orthorhombic, exhibits pseudo-hexagonal symmetry; the optical anisotropy in the $\beta\gamma$ plane is extremely small as may be seen from the values of the refractive indices $\gamma$–1·513, $\beta$–1·512, $\alpha$–1·336. This is, indeed, due to the fact that the $NO_3^-$ ions in this crystal are all oriented with their planes perpendicular to the $\alpha$-axis. Owing to this fact, only 12 spectra out of the 24 mentioned above were taken in the present study. These 12 spectra closely correspond to those of sodium nitrate studied earlier with the $\alpha$-axis substituted for the optic axis of the latter. These spectrograms are reproduced in three groups of four each (*a*, *b*, *c* and *d*) in Figs. 4, 5 and 6 corresponding to the orientations of the $\alpha$-axis along OX, OY and OZ respectively. Further, three spectra recorded with unpolarised incident light for the above orientations of the $\alpha$-axis are also reproduced in Fig. 3 (*a*, *b* and *c*). The diagram of the orientation of the $NO_3^-$ ion for the different spectrograms along with the usual notations for the nature of the vibrations of the incident and scattered light are

* In the case of $KNO_3$ these coincide with the *c*, *b* and *a* crystal axes respectively.

also given by the side of the figures. The intensities of the lines measured by the usual method of microphotometry (after making the necessary correction for the spectroscope error in the case of polarisation studies) are recorded in Tables III and IV. The values are relative to the most intense line in any particular spectrogram taken as 100. It should be pointed out here that owing to the feebleness of the lines due to the degenerate oscillations compared with the intense lattice lines, sufficiently long exposures were not given to record the former lines in all cases as they would involve the sacrifice of the details regarding the lattice lines due to over-exposure.

An inspection of the figures in the Plates shows that there is a general similarity in the behaviour of the Raman lines with orientation in sodium and potassium nitrates. Comparing Figs. 3 *a*, 3 *b* and 3 *c* when the incident light is unpolarised and the scattered light is not analysed, the most notable feature is that while the low frequency lattice oscillations are fairly of uniform intensity in all the three, the degenerate oscillations, and in particular, the line 1050 due to the symmetric oscillation of the $NO_3^-$ ion, are very weak in the third spectrogram when the plane of ion coincides with the plane containing the incident and scattered rays. This fact can be seen also when the incident light is polarised with vibrations perpendicular to the direction of observation, if we compare the aggregate intensities of the *a* and *b* components in each of the Figs. 4, 5 and 6. These facts show clearly as in the case of sodium nitrate that the polarisation due to an incident light vector perpendicular to the plane of the $NO_3^-$ ion is much less than that in the plane.

Another observation is that the low frequency lattice oscillations disappear when the internal oscillations appear strongly in the spectrum of the light scattered along the a-axis when the incident light vector is in the plane of the $NO_3^-$ ion (Figs. 5 *a* and 5 *b* taken together). However, the reverse is true for the same orientation of the crystal when the incident light vector is perpendicular to this plane (Figs. 5 *c* and 5 *d* taken together). This reciprocal behaviour can also be seen in the rest of these 12 spectrograms taken with the incident light polarised and the scattered light analysed. This spectral behaviour is strictly true for the lattice lines 82, 100 and 126 but not for the line 52 in all cases. However, it is generally clear that the changes in polarisability giving rise to these low frequency lines arise in a manner fundamentally different from those of the internal oscillations.

A particularly striking divergence in the behaviour of the lines 52 and 82 is that the former appears extremely feeble when the incident light vector is perpendicular to the plane of the $NO_3^-$ ion and also to the direction of observation (Figs. 6 *a* and 6 *b*) while the latter line appears strongly in the

TABLE III

*Incident Light Unpolarised*

| No. | $\beta$-axis oriented along | $\alpha$-axis oriented along | Vibrations of the incident light vector in | Intensities of Raman lines | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 52 | 82 | 100 | 126 | 143 | 714 | 1050 | 1343 | 1361 |
| 1 | OZ | OX | YZ plane | 45 | 100 | 13 | 15 | 4 | 12 | 70 | 7 | 7 |
| 2 | OX | OY | YZ plane | 50 | 100 | 12 | 17 | .. | 12 | 75 | 6 | 6 |
| 3 | OX | OZ | YZ plane | 50 | 100 | 14 | 15 | .. | 7 | 18 | 7 | ½ |

TABLE IV

*Incident Light Polarised*

| No. | $\beta$-axis oriented along | $\alpha$-axis oriented along | Vibrations of the incident light vector along | Intensities of components of Raman lines | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 52 | | 82 | | 100 | | 126 | | 714 | | 1050 | | 1343 | | 1361 | |
| | | | | OX | OZ | OX | OZ | OX | OZ | OX | OZ | OX | OZ | OX | OZ | OX | OZ | OX | OZ |
| 1 | OZ | OX | OZ | 30 | 4 | 100 | 7 | 10 | .. | 14 | .. | .. | 2 | .. | 60 | .. | 2 | .. | 4 |
| 2 | OZ | OX | OY | 50 | 2 | 100 | 10 | 6 | .. | 10 | .. | .. | .. | 2 | 18 | .. | 2 | .. | .. |
| 3 | OX | OY | OZ | 3 | 3 | 8 | 8 | .. | .. | .. | .. | 6 | 6 | 52 | 100 | 6 | 1 | 1 | 6 |
| 4 | OX | OY | OY | 16 | 48 | 100 | 88 | 9 | .. | 6 | .. | .. | .. | 5 | 5 | .. | .. | .. | .. |
| 5 | OX | OZ | OZ | 5 | 5 | 100 | 7 | 6 | .. | 9 | .. | .. | .. | 3 | 12 | .. | .. | .. | .. |
| 6 | OX | OZ | OY | .. | 54 | 4 | 100 | .. | .. | .. | .. | 3 | .. | 0 | 2 | 3 | .. | .. | .. |

OX component. Further the line 52 is very strong in the OZ component and weak in the OX component in the light scattered perpendicular to the $NO_3$ plane when the incident light vector is parallel to the direction of observation (Figs. 5 *c* and 5 *d*). However, the behaviour of this line is quite similar to the line 82 in all the other cases studied. The polarisation behaviour of the two lattice lines 100 and 126 is the same as that of the line 82 in all the cases where they were recorded.

Attention has already been drawn to the fact that the degenerate oscillation $\nu_2$ of the $NO_3^-$ ion appears as a doublet with frequency shifts 1343 and 1361 in this crystal. The behaviour of the split components with crystal orientation is noteworthy. Comparison of Figs. 3 *a*, 3 *b* and 3 *c* shows that with incident unpolarised light, the line 1361 practically vanishes when the plane of the $NO_3^-$ ion coincides with the plane containing the incident and scattered beams (Fig. 3 *c*) while the line 1343 appears fairly strong in the same. Further, in the spectrum of the light scattered along the $\alpha$-axis for incident light polarised with vibrations in the plane of the $NO_3^-$ ion, the 1361 line appears only in the OZ component while the line 1343 appears in the OX component (Figs. 5 *a* and 5 *b*). These and other observations on the component lines of this doublet prove, as has been shown in the next section, that the line 1361 is due to a symmetrical oscillation of the crystal and the line 1343 to an antisymmetric one. In a similar manner, polarisation studies show clearly that the line 714, though it appears in the spectrum as a single line, is due to the superposition of a symmetric and an antisymmetric oscillation of the crystal. A careful examination of the negatives seems to indicate that the component due to the symmetric oscillation has a frequency corresponding to the low frequency edge of the line and that due to the antisymmetric oscillation to its high frequency edge (in Figs. 5 *a* and 5 *b* for example). This behaviour stands in contrast to that of the doublet at 1350 where the symmetric oscillation has a higher frequency than the antisymmetric one.

### 6. *Discussion of Results*

According to Placzek (1934) the activity in Raman effect of any crystal vibration is indicated by six components $\epsilon_{ii}$ and $\epsilon_{ik}$ of the change of polarisability tensor. The surviving tensor components for any vibration can be derived from a knowledge of the symmetry properties of the vibrations and of the crystal. Accordingly an orthorhombic crystal can only have two types of vibrations (1) symmetric and (2) antisymmetric (Saxena, 1940). The symmetric oscillations are characterised by the fact that the diagonal terms of the tensor persist and the transverse terms disappear. Thus the selection rules for this type of vibraion is

$$\epsilon_{\alpha\alpha} \neq \epsilon_{\beta\beta} \neq \epsilon_{\gamma\gamma};\ \epsilon_{ik} = 0.$$

The antisymmetric oscillations are characterised by the fact that the diagonal terms are always zero. Further, these can be divided into three types:—

(1) Vibrations antisymmetric to $C_\alpha\sigma_\beta$; $C_\alpha C_\beta$; or $\sigma_\alpha$, $\sigma_\beta$ by only $\epsilon_{\alpha\beta} \neq 0$; the rest being zero.

(2) Vibrations antisymmetric to $C_\gamma\sigma_\alpha$; or $C_\gamma C_\alpha$; or $\sigma_\gamma\sigma_\beta$ by only $\epsilon_{\beta\gamma} \neq 0$; the rest being zero.

(3) Vibrations antisymmetric to $C_\gamma\sigma_\beta$; or $C_\gamma C_\beta$; or $\sigma_\gamma\sigma_\beta$ by only $\epsilon_{\beta\gamma} \neq 0$; the rest being zero.

Experimentally, these surviving tensor components for the various vibrations can be observed by studies on the Raman spectra of oriented crystals. The following equations determine the intensities of the various components in any general case.

$$P_x = \epsilon_{xx} E_x + \epsilon_{xy} E_y + \epsilon_{xz} E_z$$
$$P_y = \epsilon_{yx} E_x + \epsilon_{yy} E_y + \epsilon_{yz} E_z$$
$$P_z = \epsilon_{zx} E_x + \epsilon_{zy} E_y + \epsilon_{zz} E_z$$

where $p_x$ and $E_x$ stand for the $x$-components of the induced moment and of the incident light vector respectively. $x$, $y$ and $z$ signify the directions OX, OY and OZ respectively. For an incidence along OX, the components of the scattered radiation are along OX and OZ. Since $\rho$ the depolarisation ratio $= \frac{p_z^2}{p_z^2}$, that for an incident electric vector along OZ, $\rho = \frac{\epsilon_{zz}^2}{\epsilon_{zz}^2}$ and for an incident electric vector along OY, $\rho_y = \frac{\epsilon_{yz}^2}{\epsilon_{yz}^2}$.

In a biaxial crystal where the axes $\alpha$, $\beta$ and $\gamma$ of the optical polarisability ellipsoid have different magnitudes, for a particular orientation of the $\gamma$-axis say along OZ, the $\alpha$-axis can be either oriented along OX or along OY. In the former case, for an incident electric vector along OZ, $\rho = \frac{\epsilon_{\alpha\gamma}^2}{\epsilon_{\gamma\gamma}^2}$ and for an electric vector along OY, $\rho = \frac{\epsilon_{\beta\alpha}^2}{\epsilon_{\beta\gamma}^2}$. The corresponding values for the latter case are

$$\rho = \frac{\epsilon_{\gamma\beta}^2}{\epsilon_{\gamma\gamma}^2} \text{ and } \rho = \frac{\epsilon_{\alpha\beta}^2}{\epsilon_{\alpha\gamma}^2}.$$

The $\gamma$-axis can be also oriented along OX and OY. The polarisation and the total intensities for various orientations of the crystal thus possible are collected in Table V.

However, to determine the surviving tensor components for any vibration it is not necessary to study fully all the possible orientations of the crystal

TABLE V

| Serial No. | Orientation of the crystal | Depolarisation | | | Total intensities | | |
|---|---|---|---|---|---|---|---|
| | | Incident light vector along OZ | Light vector along OY | Unpolarised light | Light vector along OZ | Light vector along OY | Unpolarised light |
| 1 | $\alpha$ along $x$<br>$\gamma$ — $y$<br>$\beta$ — $z$ | $\frac{\epsilon_{\beta\cdot}^2}{\epsilon_{\beta\beta}^2}$ | $\frac{\epsilon_{\gamma\alpha}^2}{\epsilon_{\gamma\beta}^2}$ | $\frac{\epsilon_{\beta\alpha}^2+\epsilon_{\gamma\alpha}^2}{\epsilon_{\beta\beta}^2+\epsilon_{\gamma\beta}^2}$ | $\epsilon_{\beta\alpha}^2+\epsilon_{\beta\beta}^2$ | $\epsilon_{\gamma\alpha}^2+\epsilon_{\gamma\beta}^2$ | $\epsilon_{\beta\alpha}^2+\epsilon_{\beta\beta}^2+\epsilon_{\gamma\alpha}^2+\epsilon_{\gamma\beta}^2$ |
| 2 | $\alpha$ — $x$<br>$\gamma$ — $z$<br>$\beta$ — $y$ | $\frac{\epsilon_{\gamma\alpha}^2}{\epsilon_{\gamma\gamma}^2}$ | $\frac{\epsilon_{\beta\alpha}^2}{\epsilon_{\beta\gamma}^2}$ | $\frac{\epsilon_{\gamma\alpha}^2+\epsilon_{\beta\alpha}^2}{\epsilon_{\gamma\gamma}^2+\epsilon_{\beta\gamma}^2}$ | $\epsilon_{\gamma\alpha}^2+\epsilon_{\gamma\gamma}^2$ | $\epsilon_{\beta\alpha}^2+\epsilon_{\beta\gamma}^2$ | $\epsilon_{\gamma\alpha}^2+\epsilon_{\gamma\gamma}^2+\epsilon_{\beta\alpha}^2+\epsilon_{\beta\gamma}^2$ |
| 3 | $\alpha$ — $y$<br>$\gamma$ — $z$<br>$\beta$ — $x$ | $\frac{\epsilon_{\gamma\beta}^2}{\epsilon_{\gamma\gamma}^2}$ | $\frac{\epsilon_{\alpha\beta}^2}{\epsilon_{\alpha\gamma}^2}$ | $\frac{\epsilon_{\gamma\beta}^2+\epsilon_{\alpha\beta}^2}{\epsilon_{\gamma\gamma}^2+\epsilon_{\alpha\gamma}^2}$ | $\epsilon_{\gamma\beta}^2+\epsilon_{\gamma\gamma}^2$ | $\epsilon_{\alpha\beta}^2+\epsilon_{\alpha\gamma}^2$ | $\epsilon_{\gamma\beta}^2+\epsilon_{\gamma\gamma}^2+\epsilon_{\alpha\beta}^2+\epsilon_{\alpha\gamma}^2$ |
| 4 | $\alpha$ — $y$<br>$\gamma$ — $x$<br>$\beta$ — $z$ | $\frac{\epsilon_{\beta\gamma}^2}{\epsilon_{\beta\beta}^2}$ | $\frac{\epsilon_{\alpha\gamma}^2}{\epsilon_{\alpha\beta}^2}$ | $\frac{\epsilon_{\beta\gamma}^2+\epsilon_{\alpha\gamma}^2}{\epsilon_{\beta\beta}^2+\epsilon_{\alpha\beta}^2}$ | $\epsilon_{\beta\gamma}^2+\epsilon_{\beta\beta}^2$ | $\epsilon_{\alpha\beta}^2+\epsilon_{\alpha\gamma}^2$ | $\epsilon_{\beta\gamma}^2+\epsilon_{\beta\beta}^2+\epsilon_{\alpha\gamma}^2+\epsilon_{\alpha\beta}^2$ |
| 5 | $\alpha$ — $z$<br>$\gamma$ — $y$<br>$\beta$ — $x$ | $\frac{\epsilon_{\alpha\beta}^2}{\epsilon_{\alpha\alpha}^2}$ | $\frac{\epsilon_{\gamma\beta}^2}{\epsilon_{\gamma\alpha}^2}$ | $\frac{\epsilon_{\alpha\beta}^2+\epsilon_{\gamma\beta}^2}{\epsilon_{\alpha\alpha}^2+\epsilon_{\gamma\alpha}^2}$ | $\epsilon_{\alpha\beta}^2+\epsilon_{\alpha\alpha}^2$ | $\epsilon_{\gamma\beta}^2+\epsilon_{\gamma\alpha}^2$ | $\epsilon_{\alpha\beta}^2+\epsilon_{\alpha\alpha}^2+\epsilon_{\gamma\beta}^2+\epsilon_{\gamma\alpha}^2$ |
| 6 | $\alpha$ — $z$<br>$\gamma$ — $x$<br>$\beta$ — $y$ | $\frac{\epsilon_{\alpha\gamma}^2}{\epsilon_{\alpha\alpha}^2}$ | $\frac{\epsilon_{\beta\gamma}^2}{\epsilon_{\beta\alpha}^2}$ | $\frac{\epsilon_{\alpha\gamma}^2+\epsilon_{\beta\gamma}^2}{\epsilon_{\alpha\alpha}^2+\epsilon_{\beta\alpha}^2}$ | $\epsilon_{\alpha\gamma}^2+\epsilon_{\alpha\alpha}^2$ | $\epsilon_{\beta\gamma}^2+\epsilon_{\beta\alpha}^2$ | $\epsilon_{\alpha\gamma}^2+\epsilon_{\alpha\alpha}^2+\epsilon_{\beta\gamma}^2+\epsilon_{\beta\alpha}^2$ |

TABLE VI

| | | Calculated intensities of components of Raman lines | Observed intensities Line 1050 | Observed intensities Line 1361 |
|---|---|---|---|---|

TABLE VI

| Nature of the vibration given by the tensor component | Orientation of the crystal | Calculated intensities of components of Raman lines | | | | | Observed intensities Line 1050 | | | | | Observed intensities Line 1361 | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Incident light vector along OZ | | OY | | YZ plane | Incident light vector along OZ | | OY | | YZ plane | Incident light vector along OZ | | OY | | YZ plane |
| | | S.L.V. along | | S.L.V. along | | S.L. not analysed | S.L.V. along | | S.L.V. along | | S.L. not analysed | S.L.V. along | | S.L.V. along | | S.L. not analysed |
| | | OX | OZ | OX | OZ | | OX | OZ | OX | OZ | | OX | OZ | OX | OZ | |
| *Symmetric* | | | | | | | | | | | | | | | | |
| $\epsilon_{\alpha\alpha} \neq \epsilon_{\beta\beta} \neq \epsilon_{\gamma\gamma}$ | $\alpha-x;\ \gamma-y;\ \beta-z$ | $o$ | $l^2$ | $o$ | $o$ | $l^2$ | — | 60 | 2 | 18 | 70 | — | 4 | — | — | 7 |
| $\epsilon_{\alpha\beta}=\epsilon_{\beta\gamma}=\epsilon_{\alpha\gamma}=0$ | $\alpha-y;\ \gamma-z;\ \beta-x$ | $o$ | $m^2$ | $o$ | $o$ | $m^2$ | 52 | 100 | 5 | 5 | 75 | 1 | 6 | — | — | 6 |
| $\epsilon_{\alpha\alpha}=k,\ \epsilon_{\beta\beta}=l,\ \epsilon_{\gamma\gamma}=m$ | $\alpha-z;\ \gamma-y;\ \beta-x$ | $o$ | $k^2$ | $o$ | $o$ | $k^2$ | 3 | 12 | — | — | 18 | — | — | — | — | ½ |
| *Antisymmetric* | | | | | | | *Line* 1343 | | | | | *Line* 714 | | | | |
| | $\alpha-x;\ \gamma-y;\ \beta-z$ | $o$ | $o$ | $o$ | $n^2$ | $n^2$ | — | 2 | — | 2 | 7 | — | 2 | — | — | 12 |
| $\epsilon_{\beta\gamma}=n$, the rest being zero | $\alpha-y;\ \gamma-z;\ \beta-x$ | $n^2$ | $o$ | $o$ | $o$ | $n^2$ | 6 | 1 | — | — | 6 | 6 | 6 | — | — | 12 |
| | $\alpha-z;\ \gamma-y;\ \beta-x$ | $o$ | $o$ | $n^2$ | $o$ | $n^2$ | — | — | 3 | — | 7 | — | — | 3 | — | 7 |
| | | | | | | | *Line* 82 | | | | | | | | | |
| | $\alpha-x;\ \gamma-y;\ \beta-z$ | $p^2$ | $o$ | $o$ | $o$ | $p^2$ | 100 | 7 | 100 | 10 | 100 | | | | | |
| $\epsilon_{\alpha\beta}=p$, the rest being zero | $\alpha-y;\ \gamma-z;\ \beta-x$ | $o$ | $o$ | $p^2$ | $o$ | $p^2$ | 8 | 8 | 100 | 88 | 100 | | | | | |
| | $\alpha-z;\ \gamma-y;\ \beta-x$ | $p^2$ | $o$ | $o$ | $o$ | $p^2$ | 100 | 7 | 4 | 100 | 100 | | | | | |
| | | | | | | | *Line* 52 | | | | | | | | | |
| | $\alpha-x;\ \gamma-y;\ \beta-z$ | $o$ | $o$ | $q^2$ | $o$ | $q^2$ | 30 | 4 | 50 | 2 | 45 | | | | | |
| | $\alpha-y;\ \gamma-z;\ \beta-x$ | $o$ | $o$ | $o$ | $q^2$ | $q^2$ | 3 | 3 | 16 | 48 | 50 | | | | | |
| $\epsilon_{\alpha\gamma}=q$, the rest being zero | $\alpha-z;\ \gamma-y;\ \beta-x$ | $o$ | $o$ | $o$ | $q^2$ | $q^2$ | 5 | 5 | — | 54 | 50 | | | | | |

*Note.*—The numerical values of the intensities of lines in this table are not strictly comparative but only serve to show whether the intensities are large or small.

shown in Table V. Cases 1, 3 and 5 alone of this table have been studied in the present case of potassium nitrate. The selection rules for the symmetric and antisymmetric oscillations of the crystal enable us to predict their behaviour for the above-mentioned orientations of the crystal. Accordingly, Table VI shows the expected behaviour of the Raman lines of this crystal for transverse scattering. The observed intensities for the different lines in the spectrum for these orientations of the crystal are also entered in the same table.

The agreement in the intensities of the lines 1050 and 1361 with the theoretically expected values for the symmetrical oscillation is very close, indeed, and consequently we can assign these lines to oscillations of the symmetric type. The discrepancies found in the case of 1050 line in two of these cases may be tentatively attributed to the unavoidable experimental errors such as the effect of convergence of the incident beam and to the slight errors in orientating the crystal due to its finite size. Similar discrepancies have also been found in the cases of sodium nitrate and calcite and hence, no special mechanism need be attributed to these anomalies at present. It is to be noticed, further, that in potassium nitrate we have $\epsilon_{\beta\beta} \gtrapprox \epsilon_{\gamma\gamma}$ and is much larger than $\epsilon_{\alpha\alpha}$, so that the intensities of these symmetric oscillations are much less when the incident light vector is along $\alpha$ than along $\beta$ or $\gamma$. That the transverse components of the polarisability tensor are zero for the line 1361 is also evident from the fact that this line practically vanishes in the spectrum recorded with unpolarised incident light when the plane of the $NO_3^-$ ion coincides with the plane containing the incident and scattered beams. The behaviour of the line 1343 almost exactly corresponds to what is expected of an antisymmetric oscillation given by $\epsilon_{\beta\gamma} \neq 0$. It can be also seen from the table that the behaviour of the line 714 corresponds to a combination of a symmetric oscillation with an antisymmetric one given by $\epsilon_{\beta\gamma} \neq 0$. Thus in general, both the degenerate oscillations of the $NO_3^-$ ion actually split up into their components in the crystal with the fundamental difference that in the case of the line 1350 the frequency separation between the split components is much larger than that of the 714 line.

For the low frequency lattice line 82 it is found that the tensors for two separate autisymmetric oscillations describe the behaviour completely. Accordingly it is to be concluded that this line is due to a superposition of two oscillations given by the selection rules $\epsilon_{\alpha\beta}$ alone $\neq 0$ and $\epsilon_{\alpha\gamma}$ alone $\neq 0$. The general behaviour of the line 52 also indicates that it is also due to a superposition of two antisymmetric oscillations given by the selection rules of the same type as for the line 82. However, in this case $\epsilon_{\alpha\beta} < \epsilon_{\alpha\gamma}$ as may

be seen from the observed intensities of this line. Further, the disappearance of this line in Fig. 6 *b* is an anomaly for the above assignment and it awaits an explanation.

Analysis of the modes of oscillation of the crystal lattice of potassium nitrate shows (Bhagavantam, 1941) that out of the 18 Raman-active lattice oscillations, 6 are due to rotational oscillations of the $NO_3^-$ ions about the three principal optical directions in the crystal and the rest are due to translational oscillations. The rotational oscillations fall into four classes, $A_{1g}$, $A_{2g}$, $B_{1g}$, and $B_{2g}$. Among them, those falling under $A_{1g}$ and $B_{1g}$ correspond to oscillations of the $NO_3$ groups about the normal to their plane ($\alpha$-axis). The anisotropy in the $\beta\gamma$ plane being extremely small, these oscillations would give rise to only very faint lines. Two of the weak lattice lines observed, namely 100 and 126, might be due to these two oscillations. Their thermal behaviour also supports this assignment. The trigonal symmetry of the crystal above 129° C. causes the small anisotropy in the $\beta\gamma$ plane to disappear with the consequent disappearance of these two lines. Rotational oscillations of the $NO_3$ group about the axes $\beta$ and $\gamma$ would, however, give rise to strong Raman lines. It is possible that one of the oscillations about $\beta$ and one about $\gamma$ fall together to give the line 82 while the remaining two give rise to the line 52.

In conclusion, the author wishes to record his grateful thanks to Prof. Sir C. V. Raman for his kind advice and assistance during the progress of this investigation.

## 7. *Summary*

A careful study of the Raman spectrum of a single crystal of potassium nitrate has yielded the following frequency shifts:—52, 82, 100, 126, 143, 714, 1050, 1343 and 1361 cm.$^{-1}$ Out of these, lines 100, 126 and 143 due to the lattice oscillations of the crystal are recorded here for the first time. The most striking observation in a thermal study of the crystal is that these new lattice lines practically disappear in the spectrum of the crystal at a temperature (120° C.) just below the transition temperature (129° C.) at which the crystal changes over from orthorhombic to trigonal symmetry. The other lattice lines broaden and shift to lower frequencies with increase of temperature, while the frequency shifts due to the internal oscillations remain appreciably unaltered up to 290° C. However, the split-components 1343 and 1361 of the degenerate oscillation of the $NO_3^-$ ion broaden out and merge into one another even at 170° C. A study of the spectrum of the melt shows that there is no conspicuous change in the frequency shifts due to the internal oscillations due to change of state. A study of the effect of orientation of

the crystal relative to the directions of incidence and observation and different states of polarisation of the incident and scattered radiations shows that the behaviour of the Raman lines in this crystal satisfies the selection rules for the orthorhombic symmetry. The strong birefringence of the crystal causes the internal oscillations to appear more strongly when the incident light vector is in the plane of the $NO_3$ group than when it is perpendicular to the same. The low frequency lattice lines generally behave in a manner reciprocal to that of the internal oscillations as regards their polarisation characteristics. In the crystal each of the lines 714 and 1350 due to the degenerate oscillations of the $NO_3^-$ ion splits up into a symmetric and an antisymmetric oscillation with the difference that the separation of the split components is much larger for the latter line than for the former.

## REFERENCES


Anantakrishnan .. *Proc. Ind. Acad. Sci.*, 1937, **5**, 447.

Bär .. *Nature*, 1929, **124**, 692.

Bhagavantam .. *Proc. Ind. Acad. Sci.*, 1940, **11**, 62.

———— .. *Ibid.*, 1941, **13**, 543.

Krishnamurti .. *Ind. J. Physics*, 1930, **5**, 1.

Menzies .. *Nature*, 1929, **124**, 511.

Moses .. *Proc. Ind. Acad. Sci.*, 1939, **10**, 71.

Nedungadi .. *Ibid.*, 1939, **10**, 197.

———— .. *Ibid.*, 1940, **11**, 87.

Nisi .. *Proc. Phys. Math. Soc. Japan*, 1933, **15**, 114.

Placzek .. *Handbuch der Radiology*, **6**, Pt. II, 293–97.

Saxena .. *Proc. Ind. Acad. Sci.*, 1940, **11**, 229.

Rasetti .. *Novo Cimento*, 1932, **9**, 72.

Raman Spectra of Potassium Nitrate

Fig. 4




Fig. 5




Fig. 6

# EFFECT OF CRYSTAL ORIENTATION ON THE RAMAN SPECTRUM OF BARYTES

By T. A. S. Balakrishnan

*(From the Department of Physics, Indian Institute of Science, Bangalore)*

Received August 8, 1941

(Communicated by Prof. Sir C. V. Raman, Kt., F.R.S., N.L.)

## *1. Introduction*

The detailed study of light scattering in single crystals has assumed considerable importance in recent times on account of its relation to the theory of the solid state. The study which is conducted both with reference to the orientation of the crystal and the state of polarisation of the incident and scattered light is limited by the difficulty of obtaining a single crystal of suitable size with flawless interior and clear surfaces. In the case of barytes (barium sulphate) the natural crystal answers our purpose very well and can be obtained relatively clear and in large sizes. Barytes naturally crystallises in the di-digonal equatorial class of the orthorhombic system. According to the Dana, the Schoenflies and the Groth systems, it falls under the normal, the holohedral and the rhombic bi-pyramidal classes respectively. This crystal group requires as co-ordinate axes three lines of unequal unit lengths perpendicular to one another. The ratio of the crystallographic axes is given by $a:b:c = 0{\cdot}8152:1:1{\cdot}3136$. X-ray studies by James and Wood (1925) show that the atomic structure of barytes possesses a unit orthorhombic cell, the dimensions of which correspond, in terms of the crystal ratio to $2\,a$, $1\,b$, $1c$, *i.e.*, $1{\cdot}6304:1:1{\cdot}3136$. From the specific gravity and molecular weight of the crystal, we find the unit parallelepiped contains 4 molecules of $BaSO_4$. Of the several forms in which barytes naturally crystallises, though two were available in the collection of Professor Sir C. V. Raman, only crystals having the oblique parallelepiped habit were used in the experiments detailed below.

Despite the abundance and the ease with which crystals of barytes could be secured, it is surprising that very little work has been done on the crystal. It was therefore thought that a detailed study of the scattering in barytes with a view to secure a complete spectrum of the Raman effect would be profitable.

The results that have been obtained and are reported in this paper have justified the investigation.

## 2. *Experimental*

The investigation was carried out at room temperature (about 25° C.) with two crystals of the parallelepiped form. Of the two, the smaller crystal measured nearly 7 cm. × 6 cm. × 3 cm. and the larger 8 cm. × 6 cm. × 4 cm. The planes (001), (110) and (1$\bar{1}$0) are perfect cleavage planes in the crystal. Hence the crystal was illuminated in a direction perpendicular to the (110) plane, and the light scattered was observed in directions perpendicular to the (001) and (1$\bar{1}$0) planes. The spectrograms obtained are marked (*c*) and (*a*) respectively in Fig. 1 of the Plate. It was then illuminated along the *c*-axis which is perpendicular to the (001) plane and the scattered light observed perpendicular to the (1$\bar{1}$0) plane, and the spectrogram (*b*) in the plate was obtained.

The scattering was very weak in the crystal and it was found that exposures extending to over three days were necessary even when the Zeiss three-prism spectrograph with a short camera of focal length 12 cm. was used for securing the spectrograms. Of the three orientations, the scattering in the (*b*) orientation was fainter than in the other two cases which were nearly equal. This necessitated a longer exposure in the (*b*) orientation in order to obtain a picture of the same density as in the other two spectrograms.

## 3. *Results*

Krishnamurti (1930), Nisi (1931) and Rasetti (1931) have worked with single crystals of barium sulphate. The frequency shifts observed by them along with those of the author, obtained in the three orientations, are tabulated in Table I.

Spectrograms obtained by the use of incident unpolarised light for the three different orientations of the crystal described above are reproduced as Fig. 1 in the Plate. It is found that no particular orientation gives us the complete Raman spectrum of barium sulphate. A perusal of the table shows that fifteen shifts have been recorded for barium sulphate in all the three orientations put together. Of these the Raman line at 620 wave numbers has not been observed before. The frequency shifts at 614 and 639 wave numbers respectively observed by Nisi but not by Rasetti have been confirmed by the author who has obtained them in two out of the three orientations. But Rasetti reports a line at 631 wave numbers which the author has not obtained in any of the three spectrograms. Similarly, the Raman

TABLE I

| Direction of illumination normal to | Frequency shifts in wave numbers per centimetre | | | | | |
|---|---|---|---|---|---|---|
| | (110) | (001) | (110) | Krishnamurti | Nisi | Rasetti |
| Direction of observation normal to | (1$\bar{1}$0) | (1$\bar{1}$0) | (001) | | | |
| | 452 (5) | | | 455 | 453 | 451 |
| | | 458 (5) | 458 (5) | | | 462 |
| | | 614 (4) | 614 (4) | | 614 | |
| | 620 (4) | | | | | 631 |
| | | 638 (4) | 638 (2) | | 639 | |
| | 650 (3) | | | | | 647 |
| | 989 (10) | 989 (10) | 989 (10) | 988 | 988 | 989 |
| | | 1038 (0) | | | | |
| | | 1082 (1) | | | | |
| | 1088 (0) | | 1088 (1) | | | |
| | 1109 (1) | | | | | 1105 |
| | | 1136 (4) | | | 1139 | |
| | 1142 (2) | | 1142 (3) | | | 1141 |
| | | 1158 (2) | 1158 (1) | | | |
| | 1170 (2) | | | | | 1167 |

lines at 1038, 1082, 1088, 1136 and 1158 wave numbers respectively have not been observed before. The frequency shift of 1139 wave numbers which Nisi has recorded may be the one at 1136 wave numbers or the one at 1142 wave numbers, both obtained by the author. As against the line at 1109 wave

numbers which has come out in one of the orientations, Rasetti reports one at 1105 wave numbers. Thus six new Raman lines not reported by previous workers have been observed now.

It has been found that the relative intensities of the lines recorded in the spectra vary with the orientation of the crystal. In the orientation marked (*b*) in Fig. 1 of the Plate, the two lines with a frequency shift of 614 and 638 wave numbers have approximately the same intensity. In the other orientation marked (*c*), the line with the greater frequency shift is less intense. Variations have also been recorded in the relative intensities of the two comparatively intense lines that occur at about 1150 cm.$^{-1}$

The Raman line occurring at 452 cm.$^{-1}$ in one of the orientations and the one at 458 in the other two orientations are not separated in the spectra obtained in the present investigation, whereas Rasetti records two separate lines, in his paper, one at 451 and the other at 462 cm.$^{-1}$ A short focal length camera was used to obtain the spectra; its dispersion was not high which explains the reason for the line appearing as single. But the line at 452 wave numbers is distinct from the one at 458, since a sharp iron line divides these two positions. This can be clearly seen in the Plate.

In addition to the frequency shifts noted by Rasetti and indicated in the table, he also observed some low frequency lines between 50 and 200 cm.$^{-1}$, all of which were faint possessing an intensity of about one-tenth to one-fiftieth of the strongest line at 989 wave numbers. Some of the clear plates obtained by the author show traces of lines in the low frequency region, *i.e.*, up to about 200 cm.$^{-1}$ Unfortunately the spectrograph has a coma extending up to about 100 wave numbers and so precludes the possibility of stating anything definite about the low frequency shifts. This has evidently to be investigated with an instrument more suitable for work in this frequency region.

### *4. Results with Incident Polarised Light*

The behaviour of the Raman lines in the spectrum of barium sulphate was further investigated with the incident light polarised with its electric vector oriented parallel and perpendicular to the plane of observation. Six pictures were taken, two for each of the three orientations of the crystal described above. The intensities of these lines have been estimated visually and recorded by the side of the frequency shifts in Table II.

TABLE II

*Showing Intensities and Frequency Shifts of Raman Lines with Incident Polarised Light*

| Direction of illumination normal to | Frequency shifts in wave numbers per centimetre | | | | | |
|---|---|---|---|---|---|---|
| | (110) | | (001) | | (110) | |
| Direction of observation normal to | (001) | | (1$\bar{1}$0) | | (1$\bar{1}$0) | |
| Orientation of the electric vector with respect to the plane of observation | Parallel | Perpendicular | Perpendicular | Parallel | Perpendicular | Parallel |
| | (1) | (2) | (3) | (4) | (5) | (6) |
| | 458 (1) | 458 (3) | 458 (4) | 458 ($\frac{1}{2}$) | 452 (4) | 452 (1) |
| | 614 (1) | 614 (1) | 614 (1) | 614 (0) | | |
| | | | | | 620 (2) | 620 (2) |
| | 638 (1) | | 638 (0) | | 650 (1) | 650 (0) |
| | 989 (2) | 989 (10) | 989 (10) | 989 (2) | 989 (10) | 989 (2) |
| | 1088 (0) | | | | 1095 *b* ($\frac{1}{2}$) | |
| | 1142 (1) | 1142 (0) | | | 1142 (0) | 1142 (0) |
| | | | | 1145 *b* (0) | | |
| | 1158 (1) | | | | 1170 (0) | |

## 5. *Discussion*

Bhagavantam (1939) has remarked that the degeneracy characteristic of the tetrahedral $SO_4$ group would disappear in crystals of lower symmetry with the result that the group would have nine distinct frequencies instead of four. A further splitting into 36 modes due to the presence of four $SO_4$ groups in the lattice cell should occur, but not all of these could be expected to be Raman-active, or to be effectively resolved from each other. As will be seen from Table I, fifteen frequency shifts corresponding to the internal vibrations of the $SO_4$ group have been recorded in the present investigation with barytes, some of them differing from others only by a few wave numbers.

The selection rules enunciated by Placzek (1934) indicate two important features for the vibration spectra of crystals possessing orthorhombic symmetry. Firstly, of the eight possible vibration classes, four are allowed in

Raman effect and forbidden in the infra-red, three are forbidden in Raman effect but allowed in infra-red and one is forbidden in both. Of the four vibration classes allowed in Raman effect, one is of the symmetric type and three of the anti-symmetric type. If $\alpha$, $\beta$ and $\gamma$ represent the direction of the axes of the ellipsoid of polarisability in orthorhombic crystals, the polarisability tensor has the following six components, $\epsilon_{\alpha\alpha}$, $\epsilon_{\beta\beta}$, $\epsilon_{\gamma\gamma}$, $\epsilon_{\alpha\beta}$, $\epsilon_{\alpha\gamma}$, $\epsilon_{\beta\gamma}$. In the case of symmetric vibrations, $\epsilon_{\alpha\beta} = \epsilon_{\alpha\gamma} = \epsilon_{\beta\gamma} = 0$, while $\epsilon_{\alpha\alpha} \neq \epsilon_{\beta\beta} \neq \epsilon_{\gamma\gamma} \neq 0$. The three antisymmetric vibration classes are respectively given by only $\epsilon_{\alpha\beta} \neq 0$, only $\epsilon_{\alpha\gamma} \neq 0$, and only $\epsilon_{\beta\gamma} \neq 0$, all the other five tensor components in each case vanishing. The vibrations of the symmetric class give dipole radiation and would therefore be strongly polarised in the normal way. The vibrational modes of the anti-symmetric classes would, on the other hand, give quadrupole radiation and such lines would therefore exhibit anomalous polarisation.

The foregoing indications of theory are in general agreement with the author's results indicated in Table I setting out the experimental results for the cases wherein the incident light is unpolarised and the crystal orientation is varied, and also with those shown in Table II for similar orientations of the crystal, the incident light being polarised. Owing to the fact that the crystal used had the natural faces, two pairs of which were strongly inclined to the axes of the ellipsoid of polarisability, an assignment of all the fifteen observed frequency shifts into the appropriate vibration classes is not possible. It is clear, however, from the data and the photographs that the $\nu_1$ vibrations (989 cm.$^{-1}$) belong to the symmetric class and that the two observed components of the $\nu_2$ frequency (452 and 458 cm.$^{-1}$) should also be assigned to the same class, since both these lines exhibit a normal type of polarisation. This latter result is specially significant in view of the fact that the $SO_4$ ion in solutions shows the $\nu_2$ frequency as a completely depolarised line. The lines at 1170 and 650 cm.$^{-1}$ also are normally polarised and hence may be assigned to the symmetric class. It is noteworthy that they are the components of the higher frequency in the groups $\nu_3$ and $\nu_4$ respectively. The other Raman lines may be assigned to the anti-symmetric class since they exhibit anomalous polarisation. The subject has, however, to be further investigated with a crystal of barytes cut perpendicular to the axes of the ellipsoid of polarisability before a complete analysis of all the frequency shifts is possible.

Matossi and Kindler (1934) in investigating the infra-red spectra of barytes between 2 $\mu$ and 16 $\mu$, observed a very strong band at about 9 $\mu$ which corresponds to about 1100 wave numbers per centimetre. The author has recorded three Raman lines with shifts of about 1082, 1088 and 1109 cm.$^{-1}$

respectively lying in this frequency region. The line at 1082 cm.$^{-1}$ has appeared in one of the orientations, 1088 cm.$^{-1}$ in the other and both 1088 and 1109 cm.$^{-1}$ in the third orientation. Similarly a Raman line with a shift of 638 cm.$^{-1}$ has come out in two orientations and another line at 650 cm.$^{-1}$ in the third orientation, in the vicinity of the very strong infra-red band reported at 15·65 $\mu$ (640 cm.$^{-1}$). It should however be emphasised that the approximate correspondence noted above cannot be regarded as an identity in as much as the selection rules of Placzek demand that Raman-active oscillations should be forbidden in the infra-red and *vice versa*. No trace was found in the spectrum of the scattered light corresponding to the two weak bands at 12·35 $\mu$ (810 cm.$^{-1}$) and 10·81 $\mu$ (925 cm.$^{-1}$) in the infra-red.

Schæfer and Schubert (1916) by using two slices of barytes cut parallel to the plane containing the *a*- and *b*-axes and the *a*- and *c*-axes (the axes are given here in the crystallographic notation) have investigated the infra-red reflection maxima with radiation polarised parallel to all the three axes. With the electric vector parallel to the *a*- and *c*-axes, they obtain maxima at 8·30 $\mu$ (1204 cm.$^{-1}$) and 8·93 $\mu$ (1120 cm.$^{-1}$) respectively. On the other hand no reflection maximum is detectable with the electric vector parallel to the *b*-axis. It may be remarked that no Raman line has been observed corresponding to the 8·30 $\mu$ band in any of the spectrograms of the author. As regards the band at 8·93$\mu$, according to Schæfer and Schubert, the oscillation should appear when the electric vector is parallel to the *c*-axis and vanish altogether when it is perpendicular. The Raman line at about 1142 cm.$^{-1}$, however, behaves quite differently and has been recorded in all the six spectrograms except one where it is probable that the line has not appeared because of the extreme weakness of scattering in that setting.

The author wishes to record his grateful thanks to Prof. Sir C. V. Raman, F.R.S., for his kind interest in the work.

## 6. *Summary*

The Raman spectrum of single crystals of barytes has been studied for three different orientations. It is found that the frequency $\nu_2$ of the sulphate ion splits into two lines at 452 cm.$^{-1}$ and 458 cm.$^{-1}$ The $\nu_3$ frequency occurs as four lines at 614, 620, 638 and 650 cm.$^{-1}$ The $\nu_1$ frequency, which is the symmetric oscillation of the ion, remains single at 989 cm.$^{-1}$ The $\nu_4$ frequency splits into as many as eight components at 1038, 1082, 1088, 1109, 1136, 1142, 1158 and 1170 cm.$^{-1}$ None of the three orientations of the crystal gives the complete Raman spectrum, some of the components vanishing in particular orientations, while the intensities of the others vary. The

apparent disagreements in the results of the previous workers are thus explained. These changes have been observed using only incident unpolarised light. The Raman spectra have also been investigated with incident light polarised in and perpendicular to the plane of observation. The polarisation studies indicate that the frequencies at 452, 458, 650, 989 and 1170 should be assigned to the symmetric and the other lines to the antisymmetric class of vibrations.

## REFERENCES


Bhagavantam .. *Proc. Ind. Acad. Sci.* (A), 1939, **9**, 224.

James and Wood .. *Proc. Roy. Soc.* (A), 1925, **109**, 528.

Krishnamurti .. *Ind. Jour. Phys.*, 1930, **5**, 183.

Matossi and Kindler .. *Zeit. fur. Phys.*, 1934, **92**, 303.

Nisi .. *Jap. Jour. Phys.*, 1931, **7**, 1.

Placzek .. *Handbuch der Radiologie*, 1934, Bd. VI, Teil II, 293.

Rasetti .. *II Nuo. Cim.*, 1931, **9**, 72.

Schæfer and Schubert .. *Ann. der. Phys.*, 1916, **50**, 283.

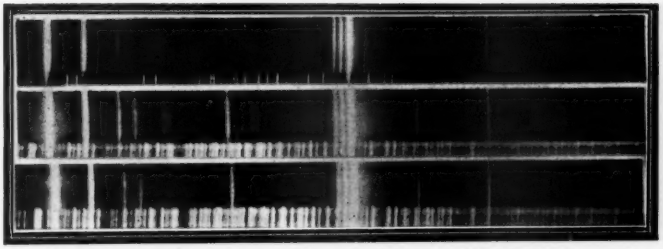



FIG. 1. Raman Spectra of Barium Sulphate in different Orientations

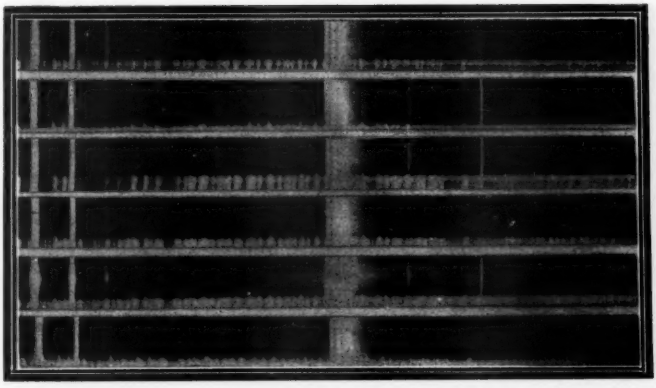



FIG. 2. Raman Spectra of Barium Sulphate with incident polarised light

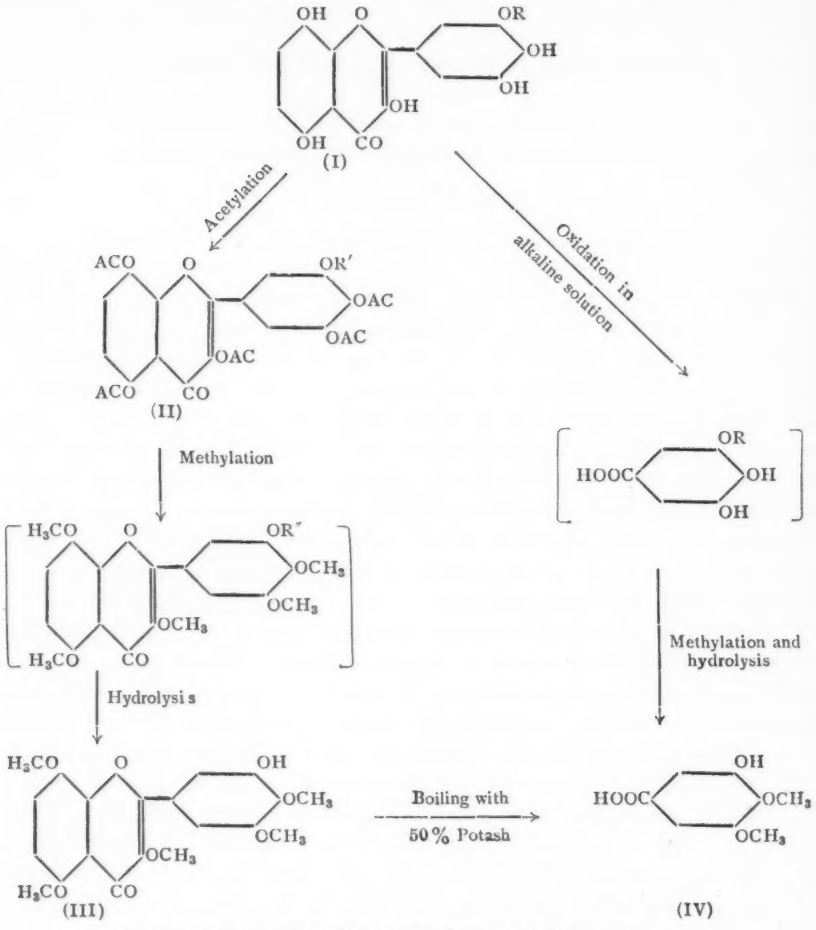
# CONSTITUTION OF CANNABISCITRIN

By P. Suryaprakasa Rao and T. R. Seshadri
*(From the Department of Chemistry, Andhra University, Waltair)*

Received August 5, 1941

It has recently been shown that the colouring matter of the flowers of *Hibiscus cannabinus* consists of a new flavonol called cannabiscetin and its glucoside, cannabiscitrin, the latter being the main component. From a study of its reactions and the degradation products, the constitution of the flavonol has been deduced to be 3:5:8:3′:4′:5′-hexahydroxyflavone.[1] Cannabiscitrin is concluded to be a monoglucoside from the combustion analysis and from the yields of the products of hydrolysis. In giving an orange-red precipitate with lead acetate and in being hydrolysed with difficulty by acids, the new glucoside ($C_{21}H_{20}O_{13}$) resembles gossypitrin, herbacitrin and quercimeritrin which carry the sugar groups in position 7, and this behaviour shows that it is not a 3-glucoside. Neither the 5- nor the 8-hydroxyl group seems to be involved in the glucoside-formation, since the substance undergoes ready oxidation to give the "gossypetone" reaction. It may, therefore, be concluded that the sugar group is present not in the benzopyrone ring but in the side phenyl nucleus. This surmise has been substantiated and the exact position involved determined in the following manner: Cannabiscitrin is completely methylated through the acetyl derivative[2] (II) and the product hydrolysed in order to remove the sugar part. When the resulting pentamethyl cannabiscetin is decomposed with boiling 50% potash, a dimethyl gallic acid is obtained. This is different from syringic acid, and found to be identical with 4:5-dimethyl gallic acid (IV). The same compound is also obtained by subjecting the glucoside to aerial oxidation in cold alkali, directly methylating the products and finally effecting the removal of the sugar molecule by acid hydrolysis. Cannabiscitrin is, therefore, concluded to be the 3′-glucoside (I), and the pentamethyl-ether mentioned above to be 3:5:8:4′:5′-pentamethyl cannabiscetin (III). The changes involved are represented diagrammatically below.

Thus cannabiscitrin is unusual amongst glycosides of flavones and flavanols in holding the glucose residue in the side phenyl nucleus. The cases so far known belonged to only two categories (1) the 3-glycosides and (2) the 7-glycosides. Recently it has been reported by us[3] that in butrin the flavanone structure carries one of the glucose units in the 3′-position, and




(R is glucose residue and R′ is the fully acetylated sugar group)

hence this type of glycosides seems to be more common than originally thought of.

## *Experimental*

*Hydrolysis of Cannabiscitrin: Estimation of the Aglucone and the Glucose.*— The glucoside (2 g.) was hydrolysed by boiling with 7% sulphuric acid (100 c.c.). After heating for a few minutes the solid went into solution, and after twenty minutes the aglucone began to separate out, giving rise to bumping. The heating was, therefore, continued on a boiling water-bath

for an hour and a half more. The contents were cooled and filtered. The filtrate was almost colourless and did not yield any appreciable amount of the aglucone on ether extraction. So the residue after the filtration was dried in air, and weighed accurately. The acid filtrate which contained the glucose was made slightly alkaline by the addition of the requisite amount of sodium hydroxide, made up to a known volume, and the sugar estimated by titration against standard Fehling solution.

The amounts of the aglucone and the glucose produced as a result of the hydrolysis of the glucoside were calculated. [Found: Aglucone, 63·4; Glucose, 33·6; $C_{21}H_{20}O_{13}$, 3 $H_2O$ requires Aglucone ($C_{15}H_{10}O_8$, $H_2O$), 62·9; Glucose, 33·7%.]

*Gossypetone Reaction with the Glucoside.*—The substance (0·5 g.) was dissolved in absolute alcohol (30 c.c.) and *p*-benzoquinone (0·2 g.) in the same solvent (2 c.c.) was added. The original solutions were both yellow in colour, and the mixture immediately assumed a dark red colour, and a dull red solid began to separate out gradually. The next day it was filtered and washed with a small quantity of absolute alcohol. It was maroon-coloured, looking like red phosphorus, and did not melt below 300°. When treated with a drop of dilute potassium hydroxide, it dissolved producing a blue solution, which became red on acidification. When the substance was suspended in water and reduced with sulphur dioxide, the original glucoside was regenerated.

*Methylation of the Glucoside and Subsequent Hydrolysis: Isolation of 3:5:8:4′:5′-Pentamethyl Cannabiscetin.*—Cannabiscitrin acetate (1 g.) was dissolved in acetone (40 c.c.) and dimethyl sulphate (10 c.c.) and 20% sodium hydroxide (10 c.c.) were added to the solution alternately in small quantities. The mixture was shaken vigorously after each addition, when it assumed a lemon yellow colour which faded gradually. Thereupon further quantities of dimethyl sulphate (5 c.c.) and the sodium hydroxide (5 c.c.) were added and finally the medium was made definitely alkaline by the gradual addition of 10 c.c. more of the above alkali. There was a gradual development of heat throughout the process, and during the later stages the mixture became so hot that there was actual boiling. After leaving overnight, it was gently boiled under reflux on a water-bath for an hour. Then almost all the solvent was driven off, the alkaline solution was just neutralised, and then sufficient amount of concentrated sulphuric acid was added so as to render the solution 7% acid. It was finally boiled under reflux for 2 hours. As no solid separated out on cooling, the contents were repeatedly extracted with ether. On evaporating off the solvent, the ether extract yielded an

almost colourless substance. When crystallised from dilute alcohol using a little animal charcoal, it was obtained as narrow rectangular plates in fern-like structures, melting at 191–92°. [Found: in the sample dried at 120° *in vacuo*: $OCH_3$, 39·7; $C_{15}H_4O_2$ (OH) $(OCH_3)_5$ requires: $OCH_3$, 40·0%.]

*Alkaline Oxidation of the Pentamethyl Ether: Isolation of* 4: 5-*Dimethyl Gallic Acid.*—The pentamethyl cannabiscetin (0·5 g.) was boiled under reflux in a silver flask with 50% potash (20 c.c.) for 6 hours. After cooling, the alkaline solution was diluted, filtered and the clear filtrate acidified with hydrochloric acid. On extraction with ether, the solution yielded a small amount of a crystalline solid which was, however, brown in colour. It was purified by dissolution in sodium bicarbonate and subsequent reprecipitation. On crystallisation from dilute alcohol, the acid was obtained as narrow rectangular plates melting at 193–95°. It was easily soluble in hot water, and the solution did not develop any characteristic colour, when treated with a drop of ferric chloride. The substance was found to be a dimethyl ether of gallic acid. [Found: $OCH_3$, 31·0; $C_6H_2$ (OH) $(OCH_3)_2$ COOH requires $OCH_3$, 31·3%.] It was not, however, identical with syringic acid (m.p. 204–05°) since the mixed melting point of the two substances was depressed and indefinite, ranging from 155–75°. All the properties indicated that the acid should be 4: 5-dimethyl gallic acid, and this was confirmed by taking the mixed melting point of the two substances; it was undepressed. For this purpose an authentic sample of 4: 5-dimethyl gallic acid was prepared from vanillin according to the method of Shriner and Mc. Cutchen.[4] Vanillin was treated with bromine in glacial acetic acid solution, when 3-bromo-vanillin was produced. It was then methylated with dimethyl sulphate and alkali to yield 3-bromo-4: 5-dimethoxy benzaldehyde, which was subsequently oxidised with alkaline potassium permanganate to form the corresponding acid. The bromine atom in this acid was finally replaced by a hydroxyl group by heating it in a sealed tube with dilute alkali and copper powder. 4: 5-Dimethyl gallic acid thus obtained melted at 193–95° and not at 184–85° as stated by Shriner and Mc. Cutchan (*loc. cit*). [Found: $OCH_3$, 31·2; $C_6H_2$ (OH) $(OCH_3)_2$ COOH requires $OCH_3$, 31·3%.]

*Further Methylation of the Pentamethyl Ether: Preparation of Hexamethyl Cannabiscetin.*—The pentamethyl cannabiscetin obtained above was dissolved in excess of 20% alkali and methylated with dimethyl sulphate in the usual manner. After the completion of the reaction, the product was acidified with dilute hydrochloric acid, and then extracted with ether. On evaporating off the solvent, a pale yellow solid was obtained. It was purified

by crystallisation from alcohol using a little animal charcoal. The substance was found to be identical with hexamethyl cannabiscetin melting at 174–75°.

*Oxidation of Cannabiscitrin: Isolation of* 4: 5-*Dimethyl Gallic Acid.* —The glucoside (1 g.) was dissolved in 50% potash (15 c.c.) and the blood red solution formed was frequently shaken and exposed to air for 24 hours. It was then diluted to about 40 c.c. and shaken with excess of dimethyl sulphate (15 c.c.) in small quantities. After leaving overnight, the mixture was heated on a water-bath for about half an hour to destroy the excess of dimethyl sulphate. The solution was still alkaline. It was therefore just neutralised with hydrochloric acid, and then the calculated amount of concentrated sulphuric acid was added so as to render the solution 7% in its acid content. It was then boiled under reflux for 2 hours, and when cooled a small amount of resin separated out. This was removed by filtration using a fluted filter, and the clear filtrate was then extracted with ether. On distilling off the ether, a brown viscous liquid was left behind. When it was left overnight in the frigidaire, an almost colourless crystalline solid separated out. It was filtered and recrystallised from boiling water using a little animal charcoal, when it appeared as colourless needles and plates melting at 192–94°. The acid was found to be identical with 4: 5-dimethyl gallic acid.

*Summary*

The final constitution of cannabiscitrin has been established. It is a monoglucoside of the flavonol cannabiscetin, carrying the sugar group in the side phenyl nucleus in the 3′-position. This has been arrived at from the following considerations:—It gives the gossypetone reaction and after complete methylation and hydrolysis, it yields a pentamethyl cannabiscetin which on decomposition produces 4: 5-dimethyl gallic acid. The same acid is also obtained by first decomposing cannabiscitrin with alkali, and then subjecting the products to methylation and subsequent hydrolysis. Thus the glucoside belongs to an unusual type and resembles butrin.

REFERENCES

1. Neelakantam, Suryaprakasa Rao and Seshadri — *Proc. Ind. Acad. Sci.*, 1941, **14**, 105.
2. Suryaprakasa Rao and Seshadri — *Ibid.*, 1939, **9**, 177.
3. ———— .. *Ibid.*, 1941, **14**, 29.
4. Shriner and Mc. Cutchan .. *J. A. C. S.*, 1929, **51**, 2193.

# KINETIC STUDIES IN ESTER HYDROLYSIS

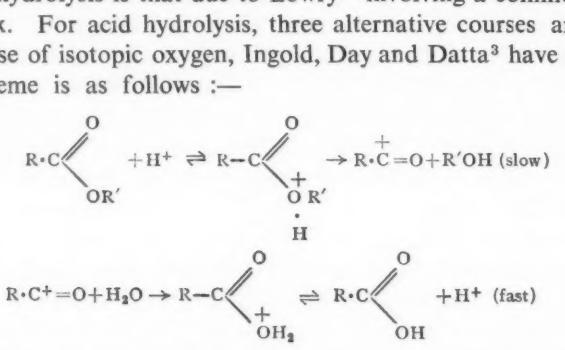
## Part I. The Hydrolysis of Halogeno-aliphatic Esters

By S. V. Anantakrishnan and S. Krishnamurti

*(From the Annamalai University Chemical Laboratories, Annamalainagar)*

Received June 10, 1941

Though the hydrolysis of esters has been the subject of study for nearly half a century since de Hemptinne's first paper,[7] it is only recently that a systematic study has been made. The accepted mechanism for both acid and alkaline hydrolysis is that due to Lowry[13] involving a common intermediate complex. For acid hydrolysis, three alternative courses are possible, but, by the use of isotopic oxygen, Ingold, Day and Datta[3] have shown that the best scheme is as follows :—




With the advent of the electronic theory, it is natural to use it in the interpretation of group influences on hydrolytic reactions as well. The susceptibility to polar influences has been well demonstrated by Kindler working with benzoic esters[12] and the more systematic and thorough studies of Ingold and Nathan,[10] Evans, Gordon and Watson[5] and Hinshelwood and co-workers.[9] It has further been noticed that in the case of meta and para substituents, the PZ values of the Arrhenius' equation remains the same while E changes with structure. Now, the activation energy may be considered to involve a repulsion term and a bond energy term in which the latter is influenced by the polar characteristics of the substituent group. Evans and Jenkins[6] were able to obtain for the hydrolysis of benzoic esters a relation of the form

$$E = E_B + E_X/\epsilon_{20}$$

where E is the activation energy, $E_B$ the bond energy and $E_X/\epsilon_{20}$ is the repulsion energy.

Most of the work generally described deals with aromatic esters while the aliphatic series seems to be comparatively neglected. It is well known that the behaviour of halogens is anomalous in the aromatic series among themselves, though they fall in the right position as regards the group as a whole. Further, it is usual to assume, since saturated carbon atoms are involved, that the influence of the halogens arises only from the transmission of the inductive effect. The present communication deals with a preliminary investigation of a few halogeno-aliphatic esters, a systematic study of which may be expected to clarify the position.

The choice of Dioxan-water as solvent needs some explanation. Usually the reaction has been studied in alcohol-water and acetone-water systems. The range of working temperature available precluded the use of acetone for any fair degree of accuracy and at the same time it was considered desirable to avoid a solvent taking part in the reverse reaction. At the same time, for comparison of results, a solvent of about the same dielectric constant and viscosity had to be chosen. The influence of the solvent is considered in greater detail in the next part. All the reactions described herein have been carried out in 60% dioxan (by weight) and the results are tabulated below (Tables I, II, III and IV).

TABLE I

*Ethyl Esters of Alkyl-substituted Acids*

| Acid | Temperature in °C. | Time for % reaction in minutes | | | | $k_1 \times 10^5$ | E (from graph) | PZ |
|---|---|---|---|---|---|---|---|---|
| | | 5 | 10 | 20 | 40 | | | |
| | 35 | 69 | 138 | 285 | 636 | 13·09 | | |
| Acetic .. | 42 | 37 | 75 | 150 | 342 | 24·41 | 16,930 | 1·47 |
| | 50 | 22 | 42 | 84 | 178 | 43·01 | | |
| | 60 | 9 | 18 | 36 | 75 | 100·2 | | |
| | 35 | 78 | 162·5 | 345 | 780 | 10·63 | | |
| Propionic .. | 42 | 45 | 87·5 | 187·5 | 425 | 19·93 | 15,960 | 0·24 |
| | 50 | 25 | 50 | 102·5 | 220 | 36·13 | | |
| | 60 | 12·5 | 25 | 51 | 110 | 68·75 | | |
| | 35 | 190 | 380 | 740 | 1600 | 4·93 | | |
| *n*-Butyric .. | 42 | 85 | 175 | 365 | 830 | 10·03 | 15,510 | 0·065 |
| | 50 | 45 | 95 | 190 | 380 | 19·36 | | |
| | 60 | 20 | 40 | 90 | 200 | 41·69 | | |

TABLE II

*Ethyl Esters of Chloro Acids*

| Acid | Temperature in °C. | Time for % reaction in minutes | | | | $k_1 \times 10^5$ | E (from graph) | PZ |
|---|---|---|---|---|---|---|---|---|
| | | 5 | 10 | 20 | 40 | | | |
| Chloracetic .. | 35 | 102 | 202 | 420 | 864 | 8·686 | 16,640 | 0·61 |
| | 42 | 60 | 120 | 240 | 522 | 15·05 | | |
| | 50 | 24 | 54 | 121 | 263 | 31·51 | | |
| | 60 | 12 | 24 | 54 | 128 | 75·27 | | |
| α-Chloropropionic .. | 35 | 234 | 468 | 1044 | 2502 | 3·763 | 15,060 | 0·20 |
| | 42 | 108 | 244 | 522 | 1170 | 7·169 | | |
| | 50 | 80 | 162 | 288 | 630 | 12·04 | | |
| | 60 | 43 | 72 | 145 | 324 | 25·09 | | |
| β-Chloropropionic | 35 | 300 | 660 | 1590 | 4380 | 2·441 | 16,070 | 0·065 |
| | 42 | 180 | 360 | 900 | 2460 | 4·516 | | |
| | 50 | 108 | 225 | 480 | 1200 | 7·785 | | |
| | 60 | 50 | 100 | 210 | 570 | 17·37 | | |

TABLE III

*Ethyl Esters of Bromo Acids*

| Acid | Temperature in °C. | Time for % reaction in minutes | | | | $k_1 \times 10^5$ | E (from graph) | PZ |
|---|---|---|---|---|---|---|---|---|
| | | 5 | 10 | 20 | 40 | | | |
| Bromoacetic .. | 35 | 72 | 165 | 378 | 888 | 10·39 | 15,780 | 0·16 |
| | 42 | 48 | 105 | 240 | 571 | 15·85 | | |
| | 50 | 27 | 54 | 114 | 270 | 32·26 | | |
| | 60 | 12 | 24 | 54 | 126 | 69·49 | | |
| α-Bromopropionic .. | 35 | 390 | 825 | 1800 | 4260 | 2·030 | 16,830 | 0·20 |
| | 42 | 240 | 465 | 945 | 2040 | 3·844 | | |
| | 50 | 90 | 225 | 480 | 1050 | 7·749 | | |
| | 60 | 60 | 114 | 225 | 504 | 16·43 | | |
| β-Bromopropionic .. | 35 | 390 | 900 | 2280 | 5400 | 1·737 | 18,690 | 3·40 |
| | 42 | 210 | 510 | 1140 | 2640 | 3·346 | | |
| | 50 | 90 | 210 | 540 | 1320 | 8·370 | | |
| | 60 | 48 | 100 | 225 | 570 | 17·37 | | |

TABLE IV

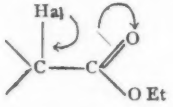
*Ethyl Esters of Iodo Acids*

| Acid | Temperature in °C. | Time for % reaction in minutes | | | | $k_1 \times 10^5$ | E (from graph) | PZ |
|---|---|---|---|---|---|---|---|---|
| | | 5 | 10 | 20 | 40 | | | |
| Iodoacetic .. | 35 | 180 | 350 | 654 | .. | 5·408 | 14,230 | 0·007 |
| | 42 | 102 | 243 | 483 | 960 | 7·460 | | |
| | 50 | 57 | 120 | 246 | 510 | 14·80 | | |
| | 60 | 24 | 57 | 111 | 228 | 32·26 | | |
| α-Iodopropionic .. | 35 | 1230 | 2280 | 4560 | 10,080 | 0·8065 | 17,260 | 0·16 |
| | 42 | 480 | 1020 | 2070 | 4230 | 1·135 | | |
| | 50 | 300 | 600 | 1200 | 2490 | 3·011 | | |
| | 60 | 120 | 276 | 510 | 1020 | 6·949 | | |
| β-Iodopropionic .. | 35 | 510 | 990 | 2250 | 5310 | 1·69 | 16,320 | 0·068 |
| | 42 | 300 | 690 | 1290 | 2850 | 2·779 | | |
| | 50 | 150 | 315 | 645 | 1380 | 5·645 | | |
| | 60 | 75 | 156 | 303 | 630 | 11·89 | | |

It will be noticed that the alkyl substituents do not affect the magnitude of the rate constant to any considerable degree but the drop in the value from ethylpropionate to ethyl butyrate is pronounced, while that from ethylacetate to propionate is slight. This change is traceable to two factors: first, the influence of the group on the formation of the transition state complex and secondly the steric factor. Alkyl groups (class + I) facilitate polarisation of the C = O bond, thereby stabilizing the complex. Further it is known from other studies that the ethyl group is a better electron-donor than the methyl. Consequently, there is a slowing down in the reaction as one ascends the homologous series, the rate tending to a more or less constant value higher up the series. This increase in stability of the activated complex is combined with a corresponding ease of formation of the complex as well. A diminishing energy of activation from ethyl acetate to ethylpropionate bears out this conclusion. The value of E also presumbly tends to a constant value in line with other properties of the aliphatic acids (*e.g.*, ionisation constant) which are influenced by polar characteristics of substituents.

The influence of the halogens is of a more complex nature. Such halogen derivatives belong to the class − I + T, the inductive and tautomeric

effects varying with the halogen. As is well known, the $-$ I effect is in the order Cl $<$ Br $<$ I. One may therefore expect that reactivity towards electrophilic reagents will diminish as one changes from the chloro to the iodo-compound. The trend in the rate constant for ester hydrolysis (*vide* Tables II, III and IV) clearly brings this out. The behaviour of ethyl bromoacetate *at lower temperatures* is somewhat anomalous. The slowest reaction among esters studied is the hydrolysis of ethyl α-iodopropionate. Now, Pauling and others have shown that the C-halogen bond possesses a certain amount of double bonded character[14] arising from resonance and this gives rise to a " conjugated system " in the α-halogeno esters.




The iodine atom is the most polarisable and one may expect from *a priori* considerations that this resonance effect will be most pronounced in α-iodopropionic ester.

Taking the halogens as a whole, the $-$ I effect diminishes the ease of formation of the activated complex while the $+$ T acts in the opposite direction. The resultant of these two opposing tendencies must account for the observed values of activation energy and rate constant. In the case of the halogeno acetates the value of E progressively decreases from the chloro to the iodo-derivative (the mono-halogeno compounds alone are considered here). On the other hand, in the case of α-halogeno propionates the position is reversed. α-Chloropropionate exhibits the lowest energy of activation while the iodo-compound shows the highest. One has to take into account, not merely, the halogen but also the alkyl group, with the result that group influences are more complex. Probably, the electron donating alkyl group attached to the same carbon atom as the halogen suppresses wholly or in part the $+$ T effect. The net result is a decrease in the ease of formation and the stability of the transition state, a slowing down of the reaction as a whole and a reversal of the relative order of the halogens. Ethyl iodopropionate is found to give the highest value for E.

The β-halogenopropionates are of a different type. An intervening saturated carbon atom, which might considerbly diminish even the inductive effect, makes the influence of the tautomeric effect on the carbethoxy group negligible. The $CH_2$ Hal. group appears essentially as an electron acceptor and the reaction becomes slow. The trend of E values shows a slight increase from the chloro to the iodo-compound.

Our attention so far has been directed to the relation between one of the Arrhenius parameters, E, and the substitutent. It is now necessary to consider the other parameter. Plotting $\log_{10} k$ against E (Fig. 1) it will be noticed

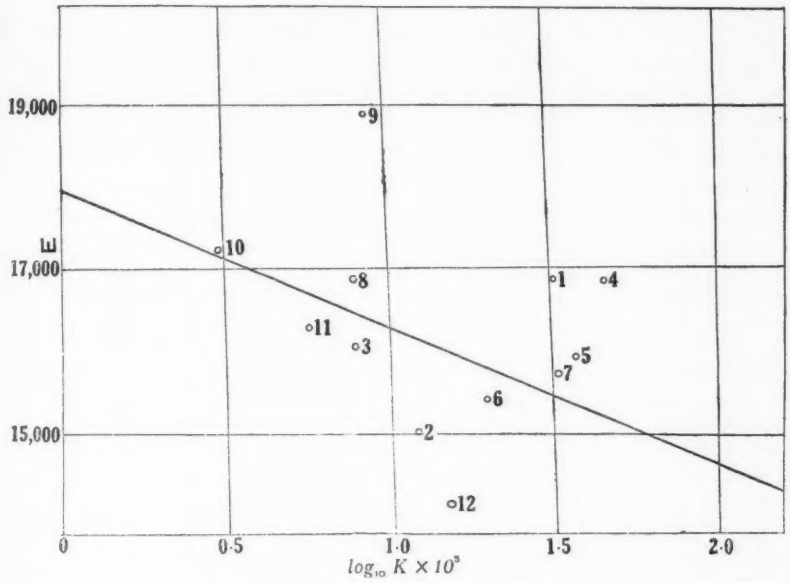



FIG. 1

KEY TO NUMBERS

1. Ethyl acetate
2. Ethyl propionate
3. Ethyl butyrate
4. Ethyl chloracetate
5. Ethyl α-chloropropionate
6. Ethyl β-chloropropionate
7. Ethyl bromacetate
8. Ethyl α-bromopropionate
9. Ethyl β-bromopropionate
10. Ethyl iodopropionate
11. Ethyl α-iodopropionate
12. Ethyl β-iodopropionate

that very few points lie along the slope $-2{\cdot}303\,RT$. Most of the points are distributed at random. This is a clear indication that the aliphatic esters studied differ on this important aspect from the aromatic compounds. The PZ values are obviously different. Now, this factor is primarily dependent on the mean molecular diameter of the interacting molecules and on the orientation of the molecule. While an increase in size increases the frequency of molecular collisions, in the present instances, this very factor appears to lead to ineffective collisions not involving the carbethoxy group. Consequently, the iodo-compound has the smallest value for this probability factor.

This same result can also be shown in another way. Hinshelwood[8] has shown that if the constant $\chi$ in the equation

$$k = \chi e^{-E/RT}.$$

were the same for all reactions, there is a linear relationship between the energy of activation and the temperature at which the reaction attains a given rate. An examination of the present series gives a random distribution of points when the E–T curve is plotted for a speed such that the reaction is half completed in one hour using the concentrations used (Table V and Fig. 2).

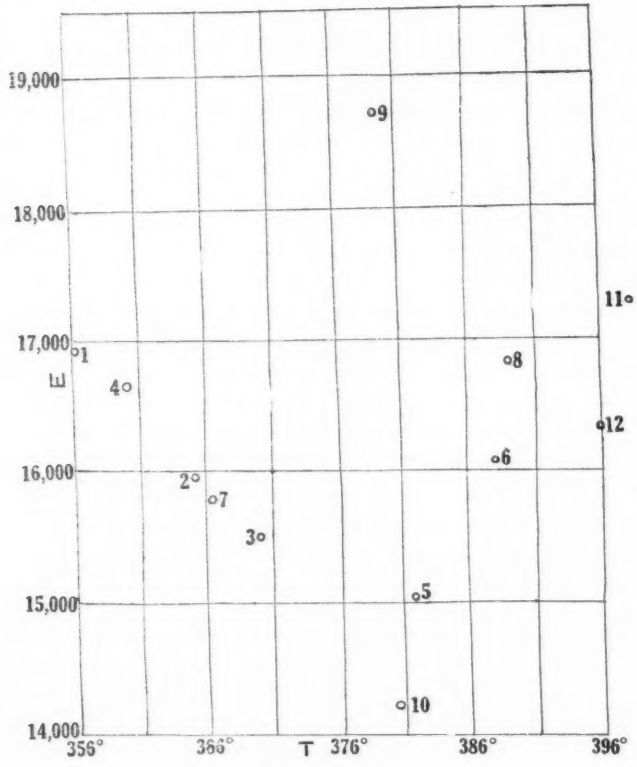



FIG. 2

E—Energy of activation in calories.
T—Temperature in degrees absolute for equal velocity of reaction.

TABLE V

| Hydrolysis of ethyl ester of acid | Temperature of equal velocity in ° absolute | Energy of activation |
|---|---|---|
| Acetic .. .. .. .. | 355·8 | 16,930 |
| Propionic .. .. .. .. | 364·9 | 15,960 |
| *n*-Butyric .. .. .. .. | 369·0 | 15,510 |
| Chloracetic .. .. .. .. | 360·0 | 16,640 |
| α-Chloropropionic .. .. .. | 381·7 | 15,060 |
| β-Chloropropionic .. .. .. | 387·9 | 16,070 |
| Bromacetic .. .. .. .. | 366·5 | 15,780 |
| α-Brompropionic .. .. .. | 387·9 | 16,830 |
| β-Brompropionic .. .. .. | 379·5 | 18,690 |
| Iodoacetic .. .. .. .. | 380·0 | 14,230 |
| α-Iodopropionic .. .. .. | 398·0 | 17,260 |
| β-Iodopropionic .. .. .. | 396·0 | 16,320 |

Any quantitative deductions on this aspect may be attempted only after a further study of a larger number of substituted aliphatic esters.

*Experimental*

Dioxan (Kodak) was purified by the method of Eigenberger[4] and the fraction, b.p., 104° C. and m.p. 11·8° C., was used. Exactly decinormal solutions of hydrochloric acid were prepared using purified dioxan diluted with 40% by weight of water.

Ethyl esters of acetic, propionic, *n*-butyric, monochloracetic, monobromacetic, α-bromopropionic and β-iodopropionic acids (Kahlbaum) were used, after purification by the usual processes, fresh samples being used for each set of experiments. Etyhl-β-chloropropionate was of Schucardt's manufacture.

Ethyliodoacetate was prepared by a modification of Kekule's method.[11] 35 Grams of ethylchloracetate was refluxed with 50 grams of sodium iodide (molar proportions) in dry acetone solution for 3 hours. After filtering of the sodium chloride, the solvent was distilled off. From the residue, the fraction boiling between 178° and 180° was taken, washed with sodium carbonate and water, dried over anhydrous sodium sulphate and fractionated. Yield 40 g. pure ester b.p. 179–80°.

Ethyl-α-chloropropionate was prepared by the method of Walker.[15] Care is needed in controlling the initial violent reaction of lactic acid with phosphorous pentachloride, but warming is needed in the later stages to complete the reaction. The pure ester boiled at 47°/20 mm.

Ethyl-α-iodopropionate was obtained by the method of Bodroux and Taboury,[1] b.p. 78°·5/28 mm.

Ethyl-β-bromopropionate was prepared by the method described in *Organic Syntheses*,[2] b.p. 65°/15 mm.

The reactions were carried out in an electrical thermostat between 35 and 60° C., the accuracy of control being ± 0·02. Air-tight, glass stoppered bottles of resistance glass were used as containers for the reaction mixture, 200 c.c. of the acid solvent was allowed to attain the temperature of the thermostat, calculated amounts of the ester for a decimolar solution added and the change with time measured acidimetrically. N/40 Baryta was used for the estimations involving unsubstituted compounds and ammonia of the same strength for the halogenated esters. The catalytic action of the acid products of hydrolysis was negligible (see also Hinshelwood *et al.*). The loss of esters by volatilisation was also inappreciable.

*Summary*

The kinetics of acid hydrolysis of some aliphatic esters have been studied at four different temperatures in 60% dioxan. The effect of the halogen on the parameters of the Arrhenius equation have been discussed from the standpoint of the electronic theory of organic reactions.

REFERENCES

1. Bodroux and Taboury .. *Comptes Rendus*, **144**, 1217.
2. Clarke, H. T. .. *Organic Syntheses* (Wiley), **3**, 58.
3. Datta, Day and Ingold .. *J. C. S.*, 1939, 838.
4. Eigenberger .. *J. Pr.*, 1931, **130**, 78.
5. Evans, Gordon and Watson *J. C. S.*, 1937, 1430; 1938, 1439.
6. Evans and Jenkins .. *Trans. Farad. Soc.*, 1940, **36**, 818.
7. de Hemptinne .. *Z. Physik. Chem.*, **13**, 561.
8. Hinshelwood .. *Kinetics of Chemical Change* (1940).
9. ——— and co-workers .. *J. C. S.*, 1937, 538; 1938, 848; 1938, 862.
10. Ingold and Nathan .. *Ibid.*, 1936, 222.
11. Kekule .. *Annalen*, **131**, 223.
12. Kindler .. *Ibid.*, 1926, **450**, 1.
13. T. M. Lowry .. *J. C. S.*, 1925, **127**, 1371.
14. Pauling .. *Nature of the Chemical Bond*, 2nd Edn. (Cornell University Press).
15. Walker .. *J. C. S.*, 1895, 919.

# KINETIC STUDIES IN ESTER HYDROLYSIS

## Part II. The Influence of Solvent on the Reaction

By S. V. Anantakrishnan and S. Krishnamurti

*(From the Annamalai University Chemical Laboratories, Annamalainagar)*

Received June 10, 1941

Though correlation between reaction in the gas phase and reactions in solution has been noticed, it is fairly established that a solvent exerts considerable influence on the course of reactions. A solvent may be termed "inert" if it is unassociated, nonpolar and chemically "saturated" and there is no difference in the rate of a reaction whether in gaseous phase or in solution. Such solvents are, however, of very limited application and are unsuitable for reactions of the type under investigation. Qualitative relationship has been established between the velocity constant of bimolecular reactions and the dielectric constant, cohesion and viscosity of the solvent.[6, 7] Using solvents of "similar type", Evans and Jenkins[1] obtain for the alkaline hydrolysis of benzoic esters the relation

$$E = E_B + E_X/\epsilon_{20},$$

where $E_B$ is the bond energy, $E_X/\epsilon_{20} = E_R$ the repulsion energy and $\epsilon$ the dielectric constant of the medium. The extent of solvent influence will naturally depend on the ratio $E_R/E$ and will be small if the ratio is too small a fraction. The solvent effect has also been thoroughly studied only in a few cases.

Now, molecules in general may exert influences on one another and, when within molecular distances from one another, there must be a pronounced change in the potential energy curves. This effect must be especially noticeable in solution. Consequently the first effect that might be observed is a difference in the energy of activation. It is also noticed that where E changes with solvent, PZ of the reaction velocity equation changes concurrently.

In Part I, the influence of substituent on the parameters of the Arrhenius equation has been considered and in the present communication attention is directed to solvent influences. Since it was considered desirable to alter both viscosity and dielectric constant, glycerol was chosen as the medium, varying amounts of water being added to alter both these physical properties.

The choice of this solvent, however, imposed a severe restriction on the choice of esters on account of their low solubility in glycerol-water systems but this does not affect the validity of the conclusions arrived at.

Three esters have been studied in four different concentrations of glycerol and at four different temperatures. For comparison, the relevant results of Part I in 60% dioxan and values calculated from the data of Hinshelwood[2] for 60% alcohol are also included. The results are summarised in Tables I–VII.

TABLE I

*Hydrolysis of Ethyl Acetate*

| Medium | Temperature in °C. | Time for % reaction in minutes | | | | $k_1 \times 10^5$ |
|---|---|---|---|---|---|---|
| | | 5 | 10 | 20 | 40 | |
| 20% Glycerol .. .. | 35 | 33·0 | 70·0 | 141·0 | 319·0 | 25·57 |
| | 42 | 20·0 | 39·0 | 78·0 | 177·0 | 47·54 |
| | 50 | 10·0 | 20·0 | 40·0 | 87·0 | 90·33 |
| | 60 | 4·5 | 9·5 | 19·0 | 42·0 | 190·1 |
| 40% Glycerol .. .. | 35 | 30·0 | 61·0 | 125·0 | 290·0 | 29·45 |
| | 42 | 15·0 | 31·0 | 67·0 | 160·0 | 56·45 |
| | 50 | 9·5 | 19·25 | 37·5 | 88·0 | 96·79 |
| | 60 | 3·5 | 7·75 | 16·5 | 39·75 | 235·7 |
| 60% Glycerol .. .. | 35 | 25·0 | 54·0 | 115·0 | 288·0 | 32·26 |
| | 42 | 11·0 | 28·0 | 63·0 | 169·0 | 60·22 |
| | 50 | 7·0 | 16·0 | 35·0 | 95·0 | 108·4 |
| | 60 | 3·5 | 8·0 | 18·0 | 47·0 | 208·4 |
| 80% Glycerol .. .. | 35 | 34·0 | 69·0 | 146·0 | .. | 25·81 |
| | 42 | 18·0 | 38·0 | 80·0 | .. | 47·26 |
| | 50 | 9·0 | 19·0 | 40·0 | .. | 93·46 |
| | 60 | 5·0 | 8·0 | 20·0 | .. | 193·6 |

TABLE II

*Hydrolysis of Ethyl Propionate*

| Medium | Temperature in °C. | Time for % reaction in minutes | | | | $k_1 \times 10^5$ |
|---|---|---|---|---|---|---|
| | | 5 | 10 | 20 | 40 | |
| 20% Glycerol .. .. | 35 | 38·0 | 72·0 | 138·0 | 307·0 | 26·31 |
| | 42 | 16·0 | 34·0 | 75·0 | 170·0 | 49·27 |
| | 50 | 9·5 | 20·5 | 40·5 | 93·5 | 88·84 |
| | 60 | 4·5 | 9·75 | 19·5 | 45·5 | 186·9 |
| 40% Glycerol .. .. | 35 | 32·0 | 62·0 | 120·0 | 284·0 | 30·80 |
| | 42 | 17·0 | 35·0 | 72·0 | 178·0 | 51·13 |
| | 50 | 9·5 | 20·0 | 40·5 | 94·0 | 90·33 |
| | 60 | 4·5 | 9·0 | 19·0 | 47·0 | 193·6 |
| 60% Glycerol .. .. | 35 | 28·5 | 57·0 | 124·5 | 321·0 | 30·10 |
| | 42 | 15·0 | 31·5 | 67·5 | 195·0 | 57·06 |
| | 50 | 7·5 | 15·5 | 35·0 | 94·0 | 110·6 |
| | 60 | 4·5 | 9·75 | 19·0 | 55·5 | 193·6 |
| 80% Glycerol .. .. | 35 | 36·0 | 72·0 | 147·0 | .. | 25·09 |
| | 42 | 15·0 | 33·0 | 80·0 | .. | 48·40 |
| | 50 | 10·0 | 22·0 | 46·0 | .. | 83·39 |
| | 60 | 4·0 | 9·5 | 21·0 | .. | 180·7 |

TABLE III

*Hydrolysis of Ethyl Chloracetate*

| Medium | Temperature in °C. | Time for % reaction in minutes | | | | $k_1 \times 10^5$ |
|---|---|---|---|---|---|---|
| | | 5 | 10 | 20 | 40 | |
| 20% Glycerol .. .. | 35 | 45·0 | 99·0 | 201·0 | 450·0 | 17·82 |
| | 42 | 27·0 | 54·0 | 112·0 | 249·0 | 32·65 |
| | 50 | 17·0 | 32·0 | 62·0 | 135·0 | 58·28 |
| | 60 | 8·0 | 16·0 | 30·0 | 66·0 | 117·9 |
| 40% Glycerol .. .. | 35 | 42·0 | 89·0 | 177·0 | 397·0 | 20·53 |
| | 42 | 25·0 | 50·0 | 100·0 | 226·0 | 36·13 |
| | 50 | 13·0 | 26·0 | 52·0 | 120·0 | 71·32 |
| | 60 | 7·0 | 13·0 | 26·5 | 61·0 | 142·7 |
| 60% Glycerol .. .. | 35 | 39·0 | 78·0 | 157·0 | 381·0 | 23·16 |
| | 42 | 21·0 | 45·0 | 96·0 | 225·0 | 38·72 |
| | 50 | 11·5 | 23·0 | 48·0 | 117·0 | 77·43 |
| | 60 | 7·0 | 13·0 | 25·0 | 61·0 | 142·6 |
| 80% Glycerol .. .. | 35 | 37·0 | 79·0 | 156·0 | 384·0 | 23·16 |
| | 42 | 21·0 | 42·0 | 90·0 | 240·0 | 43·01 |
| | 50 | 12·0 | 25·0 | 50·0 | 130·0 | 73·23 |
| | 60 | 6·0 | 12·0 | 24·0 | 62·0 | 150·5 |

TABLE IV

*Values of $k_1$, E, and Log PZ for Ethyl Acetate in Different Solvents*

| Solvent | $k_1 \times 10^5$ at 42° | E | Log PZ |
|---|---|---|---|
| 20% Glycerol .. .. | 47·54 | 16,620 | 8·2377 |
| 40% Glycerol .. .. | 56·45 | 15,870 | 7·7559 |
| 60% Glycerol .. .. | 60·22 | 14,370 | 6·7853 |
| 80% Glycerol .. .. | 47·26 | 17,100 | 8·5798 |
| 60% Dioxane .. .. | 24·41 | 16,930 | 8·1761 |
| 60% Alcohol .. .. | 17·37* | 16,200 | 7·5665 |

* The value is at 39°·8 and is taken from Hinshelwood and Timm (2).

TABLE V

*Values of $k_1$, E and Log PZ for Ethyl Propionate in Different Solvents*

| Solvent | $k_1 \times 10^5$ at 42° | E | Log PZ |
|---|---|---|---|
| 20% Glycerol .. .. | 49·27 | 15,880 | 7·7243 |
| 40% Glycerol .. .. | 51·13 | 15,250 | 7·3010 |
| 60% Glycerol .. .. | 57·06 | 13,900 | 6·4771 |
| 80% Glycerol .. .. | 48·4 | 16,130 | 7·8692 |
| 60% Dioxan .. .. | 19·93 | 15,960 | 7·3802 |

TABLE VI

*Values of $k_1$, E and Log PZ for Ethyl Monochloracetate in Different Solvents*

| Solvent | $k_1 \times 10^5$ at 42° | E | Log PZ |
|---|---|---|---|
| 20% Glycerol .. .. | 32·65 | 15,160 | 7·0414 |
| 40% Glycerol .. .. | 36·13 | 15,790 | 7·5682 |
| 60% Glycerol .. .. | 38·72 | 14,650 | 6·8325 |
| 80% Glycerol .. .. | 43·01 | 15,310 | 7·2553 |
| 60% Dioxan .. .. | 15·05 | 16,640 | 7·7993 |
| 60% Alcohol .. .. | 13·48* | 15,300 | 6·9017 |

* The value is at 39°·8 and is taken from Hinshelwood and Timm (2).

TABLE VII

| Solvent | Viscosity in centipoises at 30° C. | Time (mins.) taken for 10% reaction at 35° C. | | |
|---|---|---|---|---|
| | | Ethyl Acetate | Ethyl Propionate | Ethyl Chloracetate |
| 20% Glycerol .. .. | 1·36 | 70 | 72 | 99 |
| 40% Glycerol .. .. | 2·73 | 61 | 62 | 89 |
| 60% Glycerol .. .. | 7·31 | 54 | 57 | 78 |
| 80% Glycerol .. .. | 34·92 | 69 | 72 | 79 |
| 60% Dioxan .. .. | 1·63 | 138 | 162·5 | 202 |
| 60% Alcohol .. .. | 1·69 | 406* | .. | 445* |

* The values are at 24°·86 and are taken from Hinshelwood and Timm (2).

An examination of the tables brings out clearly that both the composition of the solvent and the nature of the ester influence the reaction. Some abnormalities are also noticeable, *e.g.*, an apparently fast reaction in 60% glycerol as compared with other concentrations of glycerol.

The most important influence that must be considered is that of the solvent on the parameters of the reaction velocity equation. It is clear that for the same reaction both E and PZ vary considerably and are affected to different degrees. The change in value of E is of the order of 2·8 kilocalories which is beyond the limits of experimental error while that in PZ is even more significant, being several powers of ten.

Following Hinshelwood and Fairclough[4] log PZ may be plotted against $\frac{1}{\sqrt{E}}$ (Fig. 1). The curves are not linear and extrapolation to $\frac{1}{\sqrt{E}} = 0$ gives for PZ values several powers of ten greater than that corresponding to

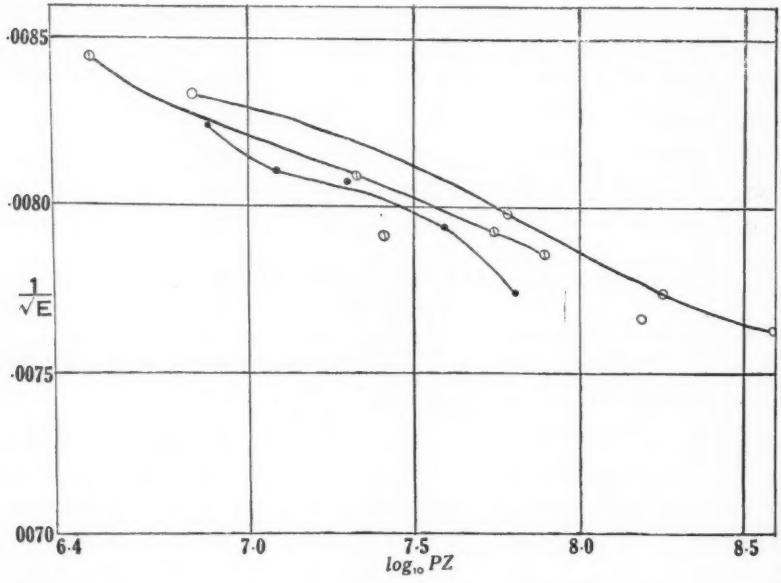



FIG. 1

a gas collision number with P = 1. At the same time the close correlation between E and PZ may be seen from the linear character of the E—log PZ curve (Fig. 2).

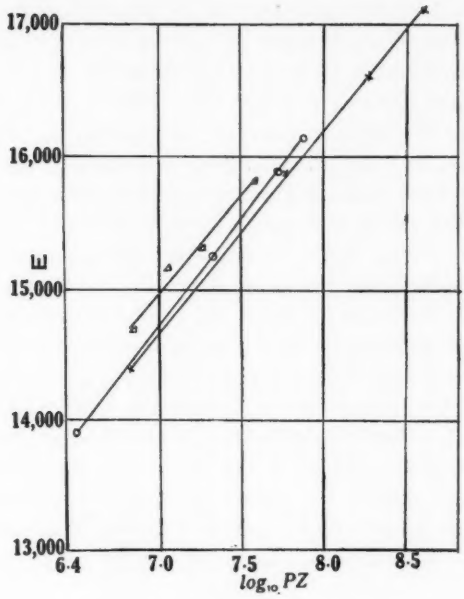



FIG. 2

○ Ethyl Acetate
× Ethyl Propionate
△ Ethyl Chloracetate

Now the whole process can be visualised as involving the principal factors of activation, deactivation and completion of the chemical change. Jowett[5] has shown that the collision frequency in a liquid system exceeds that in a gaseous system and in the derivation of the correction factor the viscosity term appears in the numerator

$$_1Z_s = \frac{3\pi\eta\sigma}{2m_1}$$

when $_1Z_s$ is the number of collisions which a solute molecule of mass $m_1$ and diameter $\sigma$ makes during one second in a medium of viscosity $\eta$.

If every collision were effective and if viscosity were to be the primary factor, one may expect the reaction in 80% glycerol to be the fastest in the present series, whereas the reaction appears fastest in 60% glycerol and the velocity in 80% glycerol is not very different from that in 20% glycerol, though the viscosity is 24 times greater. Considering the ionic nature of the reaction, the dielectric constant of solvent may be expected to greatly

influence the speed of the reaction. With glycerol-water systems, we have consequently to take into account changes in both dielectric constant and viscosity with composition. Data on the dielectric constant of mixtures of glycerol and water are not available but data on variations of viscosity with composition and with temperature are avaliable. The latter alone is inadequate for drawing any quantitative deductions, which must therefore be postponed to a later date. A qualitative comparison is, however, possible. Within the small temperature range investigated, the change in dielectric constant is only about 10% assuming the mixture law to be valid for glycerol-water systems. On the other hand, in the same range, the viscosity changes fourfold, the value at 60° being only a fourth of the value at 35°. The two influences probably work in opposite directions and one may expect a point of maximum velocity in changing from 0% glycerol to 100% glycerol. The position of this maximum will naturally shift with temperature and will vary with the nature of the ester. These changes can be observed in two ways:—(1) plotting the time taken for a definite percentage of the reaction (say 20%) against the composition of the medium (Fig. 3), and (2) plotting change of E with composition of the medium (Fig. 4).

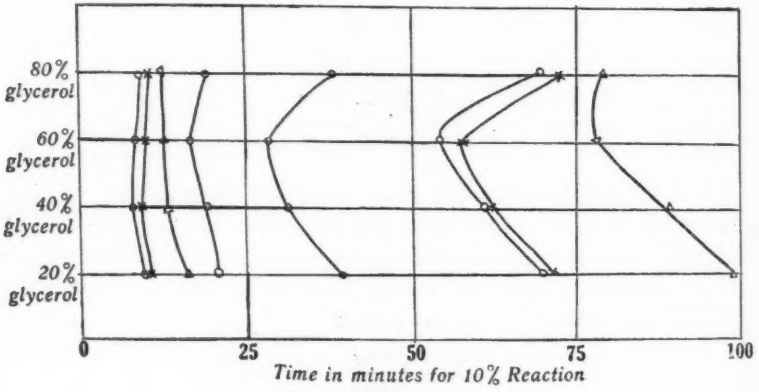



FIG. 3

○ Ethyl Acetate
× Ethyl Propionate
△ Ethyl Chloracetate

It will be noticed from Fig. 3 that a parabolic curve is obtained which flattens out with increase of temperature, the position of maximum velocity shifting from about 60% glycerol at 35° C. to 40% glycerol at 60° C. A more complete picture is possible only with larger temperature ranges and intermediate compositions for the medium.

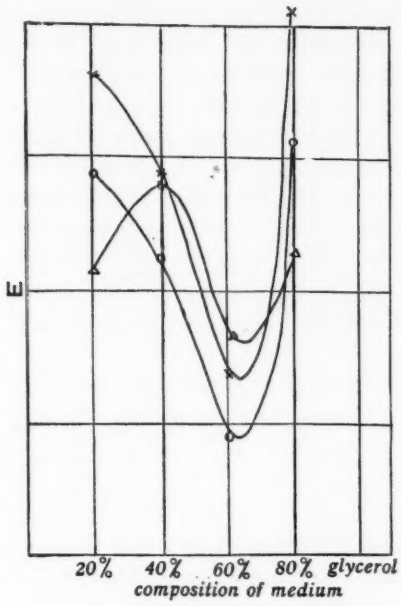



FIG. 4

Fig. 4 brings out another aspect. Ethyl acetate and ethyl propionate are affected in the same way by change of solvent. Except for a slight displacement, the shape of the curve is the same, the reaction showing a minimum value of E in the 60% glycerol region. Chloracetic ester on the other hand appears to behave differently, the curve showing a maximum and a minimum. This difference is probably only one of degree and an explanation is possible only after a more complete investigation of the change with intermediate glycerol concentrations in the solvent. These will form the subject of a later communication. The solvent influences the reaction both by increasing Z and by providing a polar environment that facilitates the breaking up of the transition-complex.

It is interesting to compare also, the velocity of the reaction in glycerol-water with that in dioxan-water and alcohol-water systems. The reaction is slowest in alcohol though the dielectric constant of alcohol is much greater than that of dioxan and the viscosity is slightly greater (Table VII). This must be attributed to the fact that ethyl alcohol is also a product of reaction and the presence of an environment of alcohol molecules stabilizes the transition complex. Since the rate-determining step involves the

breaking up of this complex, an apparently slow reaction is the result. In dioxan, this complication is absent and the reaction is much faster. Both these solvents have a lower dielectric constant and a much lower viscosity than glycerol-water systems and the comparatively faster reaction is easily understandable. Noteworthy also is the fact that though 20% glycerol is less viscous than either 60% dioxan or 60% alcohol, the reaction in that solvent is faster. The difference must be traced to the higher dielectric constant. Mention may be made here of the peculiar solvent influence in the pyridine methyliodide reaction in mixed solvents.[3]

One of the authors (S. K.) thanks the authorities of the Annamalai University for a studentship which enabled him to undertake the experimental work.

## *Experimental*

The experimental procedure was similar to that described in Part I. Glycerol (bidistilled, s.g. 1·23 for analysis, Kahlbaum) was used without further purification).

## *Summary*

The kinetics of acid hydrolysis of ethyl acetate, ethyl propionate and ethyl chloracetate in glycerol-water system has been studied. Both viscosity and dielectric constant influence the reaction and a close correlation of the parameters of the reaction velocity equation is noticed.

## REFERENCES

1. Evans and Jenkins .. *Trans. Farad. Soc.*, 1940, **36**, 818.
2. Hinshelwood *et al.* .. *J. C. S.*, 1938, 848, 862.
3. Hinshelwood .. *Kinetics of Chemical Change*, (O.U.P., 1940), 251.
4. ——— and Fairclough .. *J. C. S.*, 1937, 538.
5. Jowett .. *Phil. Mag.*, 1929, **8**, 1059.
6. Menschutkin .. *Z. Physik. Chem.*, 1890, **6**, 41.
7. Moelwyn-Hughes .. *Kinetics of Reactions in Solution*, (O.U.P., 1933), 52, 107, 117, 158.

# ISOLATION AND CONSTITUTION OF QUERCETAGITRIN, A GLUCOSIDE OF QUERCETAGETIN

By P. Suryaprakasa Rao and T. R. Seshadri
*(From the Department of Chemistry, Andhra University, Waltair)*

Received August 5, 1941

There has been some confusion in the past regarding the use of the common and the botanical names of the flowers of the Tagetes. The correct designation should be *T. erecta* for the African Marigold and *T. patula* for the French Marigold.[1]

The flowers of the African Marigold (wrongly named as *T. patula*) were first examined by Latour and Magnier De La Source.[2] They were extracted with boiling 85% alcohol, and the flavonol, quercetagetin was isolated in an impure state by concentrating the extract. Later Perkin[3] carried out a more detailed investigation. The alcoholic extract of the flowers was concentrated, diluted with water and extracted with ether which dissolved the free quercetagetin. Though Perkin realised that the aqueous solution contained a glucoside of the flavonol, he did not attempt to isolate it but directly hydrolysed it for reasons of economy to produce more quercetagetin. Thinking that Perkin and others examined the flowers of *T. patula*, Mahal[4] recently studied the flowers of *T. erecta* (wrongly designated as French Marigold) and showed that they contained the same pigment. He too did not attempt to isolate the glucoside. It is obvious that both Perkin and Mahal investigated the same species, *T. erecta*, Perkin having given the wrong botanical name and Mahal the wrong common name. This presumption of ours has been confirmed by the examination of the flowers of *T. patula* also, whose chemical composition is very different. The present investigation has been undertaken with a view to isolate the glucoside and establish its constitution, and these objects have been achieved.

The chemical examination of the petals of *T. erecta* was carried out on the same general lines as had been adopted in the case of the cotton flowers.[5] When the alcoholic extract was concentrated and allowed to stand, a yellow crystalline solid was obtained, and this was found to consist of the glucoside of quercetagetin, now called quercetagitrin. The mother-liquor was diluted with water and ether extracted, whereby quercetagetin was isolated. The

neutral and the basic lead acetate fractions were insignificant, and hence they were not worked up.

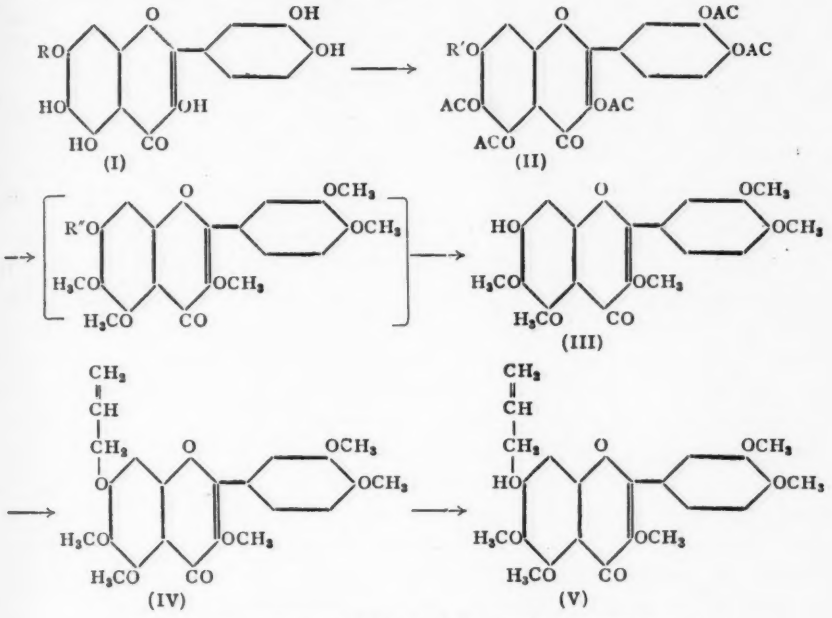
Quercetagitrin is a monoglucoside ($C_{21}H_{20}O_{13}$) yielding on hydrolysis one molecule of glucose and one of quercetagetin. It crystallises in the form of yellow needles and melts with decomposition at 236–38°. Its nona-acetyl derivative melts at 225–27°. Sodium hydroxide readily dissolves the substance to yield a yellow solution, and ferric chloride imparts a brownish-green colour to an alcoholic solution. With alkaline buffer solutions, the most prominent colour of the glucoside is pink, and this test enables the substance to be easily distinguished from its aglucone, quercetagetin which gives a transient green and a final brown or brown-red as the characteristic colours.

The new glucoside is isomeric with gossypitrin and cannabiscitrin.[6] It gives a brick-red precipitate with lead acetate and is hydrolysed with difficulty by acids, showing thereby that it is not a 3-glucoside. It undergoes ready oxidation in cold alkali to produce protocatechuic acid, and hence the sugar group should be present in the benzopyrone ring. To definitely establish its position the glucoside is completely methylated through its acetyl derivative[7] (II) and the product hydrolysed with a view to identify the resulting pentamethyl quercetagetin (III). This pentamethyl ether cannot have the free hydroxyl group in either 3- or 3′- or 4′-position since the glucoside does not have the sugar unit in those positions. Further the compound gives rise to veratric acid on oxidation in boiling 50% potash. As shown in the following table it is entirely different from 3: 6: 7: 3′: 4′-pentamethyl quercetagetin originally prepared by Perkin[3] by the methylation of the flavonol and later synthesised by Baker, Nodzu and Robinson[8] during the course of the synthesis of quercetagetin.

| | Solubility in cold sodium hydroxide | Colour with ferric chloride | Melting point |
|---|---|---|---|
| 3: 6: 7: 3¹: 4′-pentamethyl quercetagetin .. .. .. | Almost insoluble | Intense olive green colour | 159–60° |
| The new pentamethyl quercetagetin | Easily soluble | No prominent colour | 234–35° |

Hence the free hydroxyl group is not in position 5; it should be in either 6 or 7 position. To settle this point, the pentamethyl ether is allylated and the allyl ether (IV) subjected to Claisen Rearrangement, when the allyl group undergoes smooth migration (V). This is possible only if the allyl group were originally present in the 7th and not the 6th position as otherwise the

migration cannot occur for want of a free ortho- or para-position. Hence the free hydroxyl group should have been in position 7 in the pentamethyl ether and so the glucoside should be a 7-glucoside (I). The changes involved are diagrammatically represented below:




(R is glucose residue and R′ is the fully acetylated sugar group.)

## *Experimental*

*Isolation of Quercetagitrin.*—6 Kg. of the dry petals of the African Marigold flowers were extracted with methylated spirit in batches of 500 g. Each batch was refluxed with alcohol two times, each treatment lasting for about 12 hours. The combined alcoholic extract was concentrated by distillation to about 1000 c.c. The waxes and the resins that separated out were carefully filtered off through fluted filters, and after the addition of a few drops of toluene, the concentrate was allowed to stand for a long time. After four months some yellow crystalline solid began to appear. The supernatant liquid too became a thick syrup by the separation of further quantities of wax and resin, and consequently the filtration of the pigment became extremely slow and difficult. The residue which was brown in colour and sticky to the touch was thoroughly washed with alcohol, when all the impurities were removed and the solid assumed a golden yellow colour.

The mother-liquor continued to deposit more and more of the yellow substance, which was filtered at intervals, and the deposition was complete towards the end of six months. After the preliminary purification with alcohol as stated above, the compound was boiled with chloroform in order to remove carotinoid material. Now it became almost pure, and was found to be practically insoluble in boiling water, alcohol or even acetic acid, though the impure stuff readily went into solution in hot water. It was finally crystallised from aqueous pyridine, when it came out as golden yellow glistening needles and rectangular plates melting at 236–38° (decomp.). The yield was 8 g. [Found in the air-dried sample: C, 48·5; H, 4·8; $C_{21}H_{20}O_{13}$, $2\,H_2O$ requires C, 48·8; H, 4·6%. Found in the sample dried at 120° *in vacuo :* C, 52·3; H, 4·6; $C_{21}H_{20}O_{13}$ requires C, 52·5; H, 4·2%.]

*Isolation of Quercetagetin.*—The alcoholic mother-liquor remaining after the separation of the glucoside was diluted with a large volume of water and then extracted with ether. On distilling off the solvent, the extract yielded a good amount of a dark brown viscous liquid. When a small quantity of water was added, the liquid changed into a yellow crystalline solid mixed with some resin. The mixture was extracted with cold alcohol which dissolved preferentially the pigment and not the resin. On concentration the alcoholic extract deposited a yellow solid. Further purification was effected by crystallisation from acetic acid, when the substance was obtained as clusters of short needles and plates melting at 314–16°. The yield was 10 g. [Found in the air-dried sample: C, 50·5; H, 4·2; $C_{15}H_{10}O_8$, $2\,H_2O$ requires C, 50·9; H, 4·0%. Found in the specimen dried at 120° *in vacuo :* C, 56·3; H, 3·5; $C_{15}H_{10}O_8$ requires C, 56·6; H, 3·1%.] On acetylation with acetic anhydride and anhydrous sodium acetate the substance yielded an acetyl derivative which was found to melt at 209–10° and agree with acetyl quercetagetin in all its properties.

*Properties of the Glucoside.*—Quercetagitrin was obtained as fine short needles when rapidly crystallised, but on slow crystallisation, it came out as needles and narrow rectangular plates. It produced a brick-red precipitate with lead acetate, and with ferric chloride a brownish green colour. When a small quantity of sodium hydroxide solution was added, the substance immediately dissolved forming a yellow solution. On shaking with air, the yellow colour rapidly changed to brown, and a dark brown precipitate separated out. With alkaline buffer solutions of pH value below 10, the colour changes were slow and not very prominent; but with solutions of higher pH value, the characteristic colour was pink. The formation of this pink colour enables the substance to be distinguished from its aglucone

which gives on the other hand a transient green and a more stable brown or brown-red.

| pH | Quercetagetin | Quercetagitrin |
|---|---|---|
| 9·2 | Dissolved to produce a lemon-yellow solution. The colour changed to greenish-yellow within 2 minutes and greenish-brown after 10 minutes. The brown colour slowly intensified and became very prominent the next day. | Immediately dissolved forming a yellow solution. The yellow colour changed slowly to brownish-yellow and the solution assumed a brownish-pink colour after half an hour. After two hours, it was light pink which gradually intensified. After 6 hours the pink colour began to disappear slowly. Even the next day, this tinge was still noticeable. |
| 10·4 | Same changes as above but very rapid. | The same changes as above but more rapid. The brownish-yellow colour appeared after 5 minutes and changed to brownish-pink within another minute. The pink colour became prominent after 10 minutes. |
| 11·0 | An immediate lemon-yellow solution which became greenish-yellow within half a minute, greenish-brown within a minute and pure brown within 5 minutes. The transition colour between greenish-yellow and greenish-brown was pure green itself. The solution became brownish-red after half an hour and reddish-brown the next day. | The same changes as above but more quickly. The pink was very prominent even after 5 minutes. |
| 12·2 | Same changes as in the previous case but very quick. The reddish-brown appeared even within 5 minutes and changed to brownish-red after 10 minutes. | In this case the colour changes were very quick; yellow—brownish-yellow—brownish-pink—pink. The final shade was noticeable even within 3 minutes and was very prominent after 5 minutes. The next day, the solution was still pink. |

*Hydrolysis of the Glucoside.*—The substance (2 g.) was hydrolysed by boiling with 7% sulphuric acid (100 c.c.). After heating for a few minutes, the solid went into solution, and within half-an-hour another yellow solid separated out, giving rise to bumping. The contents were, therefore, heated for an hour and a half more on a boiling water-bath. After cooling, the precipitate was filtered and the filtrate extracted with ether to completely recover the aglucone. The ether-extract, after the distillation of the solvent, yielded a small amount of the substance. The two samples of the aglucone were mixed together, dried in air and weighed accurately. After recording the yield, the solid was crystallised from dilute alcohol, when it came out as short needles and plates melting at 315–16°. [Found in the air-dried sample: C, 50·5; H, 4·0; $C_{15}H_{10}O_8$, 2 $H_2O$ requires C, 50·9; H, 4·0%.]

The substance was identified as quercetagetin and this was confirmed by preparing its acetyl derivative and comparing it with an authentic sample of acetyl quercetagetin.

The acid solution left after the removal of the aglucone was made up to 120 c.c. and divided into two equal portions. One part was further diluted, neutralised with barium carbonate, and treated after concentration to a small bulk with phenyl hydrazine in dilute acetic acid. When the mixture was heated on a water-bath, the osazone separated out. After crystallisation from alcohol, it was identified as glucosazone from a study of its crystalline structure and the melting point (204–06°). The other part of the sugar solution was made alkaline by the addition of sodium carbonate and the glucose estimated by titration against standard Fehling solution.

The amounts of the aglucone and the glucose produced as a result of the hydrolysis of the glucoside were calculated. [Found: Aglucone, 68·0; Glucose, 34·3%; $C_{21}H_{20}O_{13}$, $2\,H_2O$ requires: Aglucone ($C_{15}H_{10}O_8$, $2\,H_2O$) 68·6; Glucose, 34·9%.]

*Alkaline Oxidation of the Glucoside*: *Isolation of Veratric Acid.*—Quercetagitrin (0·5 g.) was treated with 50% aqueous potash (15 c.c.), when it dissolved immediately to form a blood-red solution. On leaving exposed to air with occasional shaking for 24 hours, the solution became opaque and brown. It was then directly treated, after dilution, with excess of dimethyl sulphate (20 c.c.) in small quantities. After shaking for an hour, the contents were heated on a water-bath for about 30 minutes to complete the methylation and decompose the excess of the methylating agent. The solution was then acidified and ether extracted. A crystalline solid was obtained on evaporating the solvent from the ether extract. It was purified by dissolving in sodium bicarbonate solution and precipitating with hydrochloric acid. When crystallised from aqueous alcohol, it was obtained as colourless needles melting at 183–84°, and was found to be identical with veratric acid.

*Acetylation of the Glucoside*: *Nonaacetyl Quercetagitrin.*—A small quantity of the glucoside was acetylated by boiling with acetic anhydride and anhydrous sodium acetate. The acetyl derivative was crystallised from glacial acetic acid, when it was obtained as colourless needles melting at 225–27°. [Found: C, 54·8; H, 4·8; $C_{21}H_{11}O_4$ $(OCO\ CH_3)_9$ requires C, 54·5; H, 4·4%.]

3 : 5 : 6 : 3′ : 4′-*Pentamethyl Quercetagetin.*—The acetyl quercetagitrin (0·5 g.) was dissolved in acetone (25 c.c.) and treated alternately with dimethyl sulphate (10 c.c.) and 20% sodium hydroxide (10 c.c.) in small quantities,

The mixture was shaken vigorously after each addition; considerable amount of heat developed during the course of the reaction. Further quantities of the methylating agent (5 c.c.) and the alkali (5 c.c.) were then added, and finally the medium was made definitely alkaline by the gradual addition of more alkali (15 c.c.). The next day the mixture was refluxed for an hour on the water-bath, and the acetone present was then distilled off. Subsequently the clear alkaline solution was just neutralised and then the required amount of concentrated sulphuric acid was added to it so as to make it 7% in the acid content. After boiling under reflux for 2 hours, the clear solution was cooled in the refrigerator, when a colourless crystalline solid was deposited. It was filtered and the filtrate on ether-extraction yielded a little more. On crystallisation from dilute alcohol, it was obtained as long plates and needles melting at 234–35°. It was easily soluble in sodium hydroxide and it gave no colour with ferric chloride. The yield was 0·3 g. [Found: C, 61·8; H, 5·3; $OCH_3$, 39·4; $C_{15}H_4O_2$ (OH) $(OCH_3)_5$ requires C, 61·9; H, 5·2; $OCH_3$ ,40·0%.] By subjecting it to alkaline oxidation using boiling 50% aqueous potash in a silver flask, the pentamethyl ether gave rise to veratric acid.

3′: 4′: 3: 5: 6-*Pentamethyl-7-allyl Quercetagetin.*—The pentamethyl quercetagetin (0·5 g.) was dissolved in dry acetone (50 c.c.), anhydrous potassium carbonate (2 g.) and excess of allyl bromide (2 c.c.) were added to the solution and the mixture boiled under reflux on a water-bath for about 6 hours. The potassium salts were then filtered off and all the solvent was completely removed by distilling the clear solution, when a brown-coloured oil was left behind. It was dissolved in ether, and the solution extracted with 5% sodium hydroxide to remove any unattacked pentamethyl quercetagetin. On the removal of the solvent, the ethereal solution yielded again only an oil, which, however, was much less coloured and turned solid after the addition of a little water and leaving overnight in the ice-chest. It was finally purified by crystallisation from dilute alcohol using a little animal charcoal, and was obtained as almost colourless needles. It sintered at about 118° and melted at 122–24°. [Found in the sample dried at 120° *in vacuo*: C, 64·2; H, 5·7; $C_{23}H_{24}O_8$ requires C, 64·5; H, 5·5%.] The compound did not dissolve in dilute sodium hydroxide and gave no colour with ferric chloride. The yield of the pure product was 0·3 g.

3′: 4′: 3: 5: 6-*Pentamethyl-8-allyl Quercetagetin.*—The above pentamethyl-7-allyl quercetagetin (0·3 g.) was taken into a pyrex filter-tube provided with a tight-fitting rubber stopper. The tube was then exhausted as much as possible using a "Cenco" pump for 15 minutes and then heated on

an oil-bath at 195–200° for 1½ hours. By this treatment a brown semi-solid was obtained, which completely solidified on the addition of a small quantity of water. It crystallised from dilute alcohol (animal charcoal) as colourless narrow rectangular plates melting at 188–90°. [Found: C, 64·2; H, 5·8; $C_{23}H_{24}O_8$ requires C, 64·5; H, 5·5%.] It was freely soluble in dilute sodium hydroxide. The yield of the pure substance was 0·2 g.

*Summary*

Quercetagitrin, a monoglucoside of quercetagetin, has for the first time been isolated from the flowers of the African Marigold (*Tagetes erecta*). It is not a 3-glucoside since it gives a red precipitate with lead acetate and does not undergo easy hydrolysis with acids. Further it is easily oxidised in cold alkali, and after methylation the products of decomposition yield veratric acid. The glucose group, therefore, is not present in the side phenyl nucleus. By complete methylation and subsequent hydrolysis of the glucoside, a pentamethyl quercetagetin is obtained. This ether is a new compound, and differs from 3:6:7:3′:4′-pentamethyl quercetagetin in all its properties, and hence the free hydroxyl group in it is in either the 6th or the 7th position. The allyl ether of this new pentamethyl quercetagetin smoothly undergoes the Claisen Rearrangement, indicating thereby that the ortho-position with respect to the allyloxy group is unsubstituted. Hence the allyl ether should be 3:5:6:3′:4′-pentamethyl-7-allyl quercetagetin, and the new pentamethyl ether should have the constitution of 3:5:6:3′:4′-pentamethyl quercetagetin. Consequently quercetagitrin is the 7-glucoside of quercetagetin.

REFERENCES

1. (*a*) .. *Firminger's Manual of Gardening for India*, 7th Edition, Revised and Edited by W. Burns, 477.
   (*b*) .. *The Treasury of Botany*, 1120.
2. Latour and Magnier De la Source .. *Bull. Soc. Chim.*, 1877, (ii) **28**, 337.
3. Perkin .. *Proc. Chem. Soc.*, 1902, **18**, 75; *J. C. S.*, 1913, **103**, 209.
4. Mahal .. *J. I. C. S.*, 1938, 87.
5. Neelakantam, Ramachandra Rao and Seshadri *Proc. Ind. Acad. Sci.*, 1935, 2, 490.
6. ——— Suryaprakasa Rao and Seshadri .. *Ibid.* 1941, **14**, 105.
7. Suryaprakasa Rao and Seshadri .. *Ibid.*, 1939, **9**, 177.
8. Baker, Nodzu and Robinson *J. C. S.*, 1929, 74.

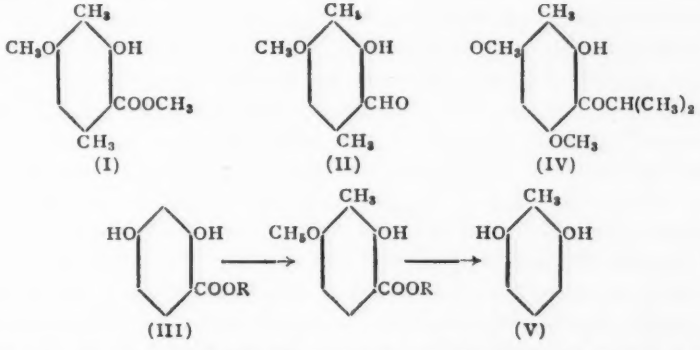
# NUCLEAR METHYLATION OF β-RESORCYLIC ALDEHYDE

By T. R. Seshadri and V. Venkateswarlu

*(From the Department of Chemistry, Andhra University, Waltair)*

Received August 5, 1941

Under conditions of methylation, certain poly-hydroxy phenyl derivatives exhibit a tendency to undergo substitution in the benzene nucleus. This phenomenon is known as nuclear methylation. Not only is the chemistry of this reaction interesting, but it has also useful applications in synthetic work. For instance, methyl orsellinate was found to be directly and conveniently methylated with the formation of methyl rhizonate[1] (I). In a similar manner rhizonic aldehyde (II) has been prepared readily by the methylation of orcylic aldehyde. Early work of Perkin[3] and of Herzig *et al.*[4] on the methylation of β-resorcylic acid and ester (III) has been reviewed in the above-mentioned paper by Robinson and Shah.[1] Their ideas have been confirmed by Jones and Robertson[5] by careful comparison of some of the important products of methylation with substances obtained by definite methods of synthesis.

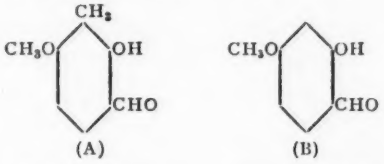



Kauffler[6] and Perkin[3] found that nuclear ethylation is a much less facile process. Robinson and Shah,[1] however, were able to effect nuclear ethylation of the methyl ester of resorcylic acid using large excess of the reagents. Nuclear methylation of resocetophenone was effected by Greger,[7] Wechler[8] and Crabtree and Robinson[9] and nuclear ethylation was carried out by Robinson and Shah.[1] The constitution of the products was drawn only

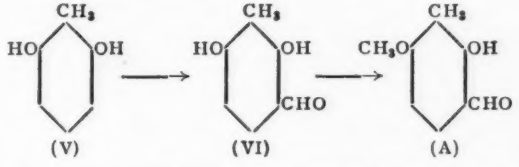
from analogy with the similar reaction with resorcylic acid and ester. The subject was subsequently reinvestigated by Rangaswami and Seshadri,[10] who confirmed the structures by unequivocal synthesis and by preparation of derivatives. They employed for this purpose resacetophenone and ω-methoxy-resacetophenone. An observation regarding nuclear methylation of a phloroglucinol derivative has been recently made by Hems and Todd.[11] Using phloroisobutyrophenone, they found that the reaction took place even under very mild conditions by boiling the substance in acetone solution with methyl iodide and potassium carbonate; bæckeol (IV) was thus obtained. This may be taken as an instance of very facile nuclear methylation.

The following is an account of past work relating to the nuclear methylation of β-resorcylic aldehyde. Tiemann and Parrisius[12] obtained a compound (A) melting at 62–63° by two methods: (i) by the action of chloroform and alkali on mono-methyl resorcinol, and (ii) by the methylation of β-resorcylic aldehyde with methyl iodide and alcoholic potash. They assigned to it the structure of 2-hydroxy-4-methoxy-benzaldehyde and this has been shown to be wrong by subsequent work. Claisen and Eisleb[13] showed that by employing methyl iodide and potassium carbonate for the methylation of β-resorcylic aldehyde, two compounds could be isolated: (i) melting at 62–63° and identical with (A) and (ii) melting at 41–42° (B). The mixture of these two products could be separated by taking advantage of their difference in volatility with steam under different conditions; compound (A) distilled over from a faintly alkaline solution and subsequently after rendering the solution acid, compound (B) could be distilled. The above work was confirmed by OTT and Nauen[14] who further showed that methylation of β-resorcylic aldehyde with methyl iodide and alcoholic potash gave compound (A) along with a small quantity of (B), whereas when dimethyl sulphate or methyl bromide and aqueous potash were employed, compound (B) was exclusively formed. The constitution of compound (B) was established by them as 4-O-methyl-resorcylic aldehyde from careful elementary analysis and comparison with a sample obtained from natural products (*e.g.*, from the root of chlorocodon from Natal isolated by Goulding and Pelly).[15] It is now known to occur widely in the following plants: (i) *Decalepis Hamiltonii* (Srinivasa Rao and Sesha Iyengar[16]); (ii) *Periploca Gracea* (Solacoln, Mavrodin and Hermann[17]); (iii) *Hemidesmus indicus* (Dutta, Ghosh and Chopra[18]). Compound (A) was subsequently taken to be nuclear methylated homologue of (B) and it was assumed to have the structure of 2-hydroxy-3-methyl-4-methoxy-benzaldehyde; this assumption was based on analogy with similar resorcinol derivatives. Its formation in small amounts in the experiments of Tiemann and Parrisius[12] using chloroform, alkali and mono-methyl resorcinol was

difficult to explain. OTT and Nauen[14] were of the opinion that the monomethyl resorcinol employed by these authors probably contained 2-methylresorcinol. But the explanation does not seem to be satisfactory and the original observations may require revision.

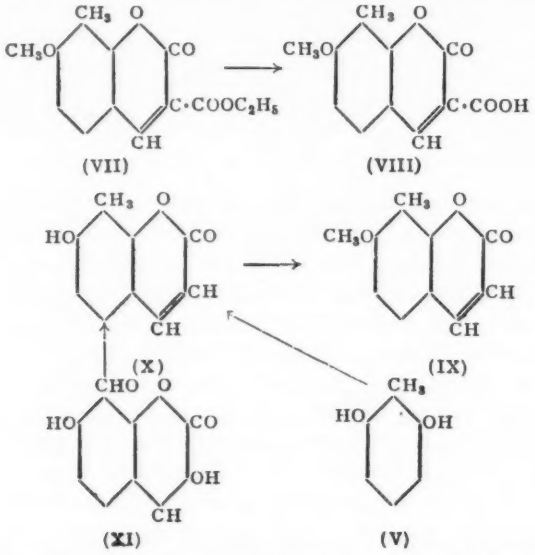



The methods employed by previous workers for effecting nuclear methylation of β-resorcylic aldehyde have not yielded satisfactory results and the constitution of the product has not been established by independent synthesis. OTT and Nauen[14] treated a solution of β-resorcylic aldehyde and methyl iodide in methyl alcohol with finely powdered potassium hydroxide during the course of 12 days. They obtained compound (A) in low yields and it had to be separated from a small quantity of 4-O-methyl-resorcyclic-aldehyde. A rapid and convenient procedure has now been worked out and under these conditions (see experimental part) only one product, compound (A) melting at 64–65°, is obtained. The constitution of this compound, as 2-hydroxy-3-methyl-4-methoxy-benzaldehyde has been established by two independent methods: (i) it has been synthesised, starting from 2-methylresorcinol (V) according to the method of Jones nd Robertson[5] and the synthetic product compared with the sample obtained by methylation of β-resorcylic aldehyde. The two are identical.

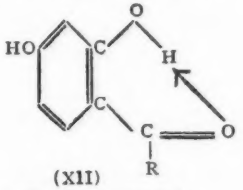



(ii) Compound (A) was condensed with diethyl malonate using piperidine as the condensing agent. The coumarin-3-carboxylic ester (VII) thereby obtained was hydrolysed and the product (VIII) decarboxylated. The final coumarin (IX) thus obtained was found to be 8-methyl-7-methoxy-coumarin, by comparison with a sample obtained independently by synthesis as given below. 2-Methyl-resorcinol (V) was condensed with malic acid to form 8-methyl-7-hydroxy-coumarin (X). The same compound was also obtained by the reduction of 8-aldehydo-7-hydroxy-coumarin (XI) (Spaeth[18]) with hydrogen using palladium charcoal as catalyst. It readily underwent

methylation with methyl iodide and potassium carbonate to yield 8-methyl-7-methoxy-coumarin (IX). Thus it is clear that the nuclear position involved in the methylation of $\beta$-resorcylic aldehyde is position 3, and that of the two hydroxyl groups, only that present at 4 undergoes ether formation.




In the examples of nuclear methylation discussed in the previous pages, it should be noted that they come under the category of polyhydroxy carbonyl compounds. The same characteristics of the reactions are observed throughout. Nuclear position 3 with respect to the carbonyl group is the reactive one. Regarding the hydroxyl groups, one of these ortho to the carbonyl group is left unmethylated. It is well known that all these hydroxy-carbonyl compounds are chelated and this chelation has a tendency to cause fixation of the benzene double bonds as shown in (XII).



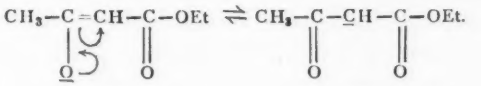

(XII)

(R = H, $CH_3$ or $OCH_3$)

The existence of chelation may account for the non-methylation of the ortho-hydroxyl group and it may also explain the high reactivity of position 3.

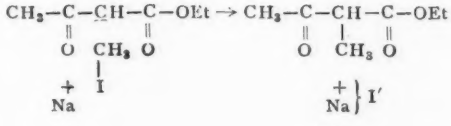
From a study of the nuclear methylation of resacetophenone, Crabtree and Robinson[9] have advanced the following regarding the mechanism of the reaction. These authors indicated that the nuclear methylation of resacetophenone is a reaction of the alkali metal derivatives of the original ketone itself (not of paeanol, the mono-methyl ether) and that it is favoured by an excess of alkali. They found that 4-O-methyl-resacetophenone does not undergo nuclear methylation under the above conditions.

The analogy between the above nuclear methylation and the C-alkylation of ethyl-aceto-acetate seems to be obvious. In both cases the primary cause of the reaction is the existence of an anionoid carbon atom. In the presence of sodium (or potassium) alkoxide the following (E) and (K) may be said to be in equilibrium when ethyl-aceto-acetate is involved.



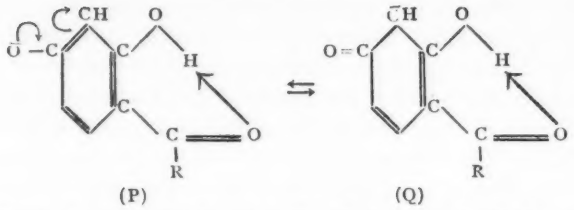
(E) (K)

Though (K) may be the lesser component owing to the higher reactivity of the amonoid carbon as compared with the more stable anionoid oxygen, reaction with methyl iodide takes place predominantly with (K) leading to C-methylation (M).



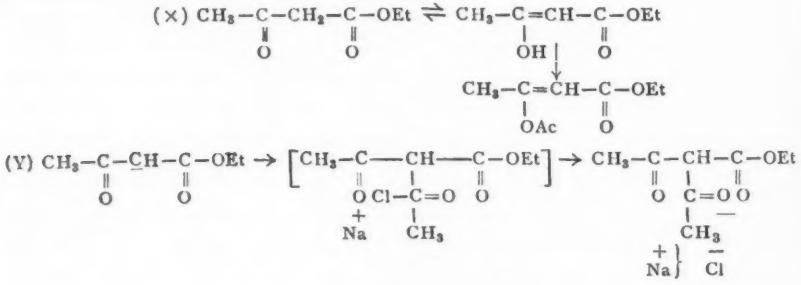
(M)

In the case of carbonyl derivatives of resorcinol as shown in (XII), the existence of an extra double bond between the C = O and the carbon atom concerned in no way alters the situation. Under the conditions of methylation adopted (P) and (Q) are obviously in equilibrium and nuclear methylation takes place quite analogous in mechanism to that just outlined, with the only difference that the hydrogen attached to the 3 carbon finally migrates to the oxygen to give a phenol. This explains why preliminary methylation of the para-hydroxyl group is injurious to nuclear methylation (Crabtree and Robinson[9]). Further it may be remarked that existence of chelation may be expected to increase the electron pull towards the carbonyl, thus facilitating the polarisation as indicated in (P) and eventually nuclear methylation. The conditions employed seem to be very conducive for the existence of chelate structure, thus preventing the methylation of the ortho-hydroxyl group.



(P) (Q)

It has been the practice to view C- alkylation of ethyl-aceto-acetate as involving addition of methyl iodide at the double bond of the enol.[20] This does not seem to be tenable since there is no positive proof of such addition and since there is no other example where methyl iodide has been proved to add on to the double bonds. On the other hand, all its reactions seem to be characterised by the ready elimination of iodide ions after attack at the unstable anionoid carbon. In this connection it may be mentioned that acid chlorides react with the sodium derivative of ethyl-aceto-acetate similarly to form C-acyl derivatives whereas when the free compound itself is employed in the presence of pyridine O-acyl derivatives are formed.[21] The latter is obviously simple ester formation in which the enol takes part and the keto-isomer is unreactive (X). The reaction with the metal derivative is again due to attack on the anionoid carbon (Y). Definite cases of addition of acyl chlorides to double bonds are not known.



## *Experimental*

*Nuclear methylation of β-resorcylic aldehyde*: *2-hydroxy-3-methyl-4-methoxy-benzaldehyde* (*A*).—To a solution of caustic potash (7·5 g., 4·5 mols.) in anhydrous methyl alcohol (40 c.c.) β-rescorcylic aldehyde (5 g.) was added. The solid dissolved slowly to form a clear solution which was deep brown in colour. On cooling it in a freezing mixture, it set into a solid mass. Enough methyl alcohol was therefore added to obtain a clear solution again at this low temperature and then the mixture was treated with excess of ice-cold methyl iodide (30 c.c., 7 mols.) in one lot.

The contents were then well shaken for about half an hour, the flask being immersed in freezing mixture and kept well-stoppered. Subsequently it was allowed to assume laboratory temperature slowly and to stand overnight. Next morning, crystals of potassium iodide had separated at the bottom and a clear solution was found above. The mixture was gently boiled under reflux for 8 hours, cooled and poured into ice-water and left overnight. As much of the alcohol as possible was then removed by distillation under reduced pressure and the highly coloured residue was subjected to steam-distillation. A colourless oil came over and soon solidified. When recrystallised from methyl alcohol it was obtained as colourless elongated rectangular plates melting at 64–65°. [Found: C, 64·9; H, 6·2; $C_9H_{10}O_3$ requires C, 65·1; H, 6·0.] The yield of the pure product was 1·5 g. It does not undergo condensation with acetic anhydride and sodium acetate under the conditions of Perkin's reaction.

2:4-*Dihydroxy*-3-*methyl-benzaldehyde* (*VI*): was made according to the method of Jones and Robertson with the modification that zinc cyanide was used in the place of hydrogen cyanide.

A solution of 2-methyl resorcinol (2 g.) and zinc cyanide (5 g.) in anhydrous ether (40 c.c.) was cooled in ice and saturated with hydrogen chloride. The aldimine hydrochloride began to separate after thirty minutes. The current of the gas was, however, continued for 4 hours, at the end of which the solid was separated, washed with more ether and decomposed with water (35 c.c.) by heating on a boiling water-bath. The aldehyde separated out from water in colourless rhombic prisms melting at 150° with slight sintering at 137°. The yield of the product was 1·6 g.

The above dihydroxy-aldehyde (VI) was methylated using excess of methyl iodide and potassium carbonate in boiling acetone solution. Almost quantitative yield of the 4-methyl ether was obtained and it crystallised from dilute alcohol in plates melting at 64–65°. It was found to be identical with the sample obtained from the nuclear methylation of β-resorcylic aldehyde.

*Ethyl*-7-*methoxy*-8-*methyl-coumarin*-3-*carboxylate* (*VII*).—The nuclear methylation product (A) (1 g., 1 mol.) was mixed with diethyl malonate (1·4 g., 1·4 mol.) and cooled in ice. Piperidine (10–15 drops) was then added. (Cooling was found necessary as otherwise heat was developed causing considerable resinification.) The mixture was allowed to stand overnight and to attain room temperature slowly. The resulting solid was treated with dilute hydrochloric acid, filtered and recrystallised from alcohol. It came out as colourless thin rectangular plates melting at 159–60°. In neutral alcoholic solution it emitted a violet fluorescence and in concentrated

sulphuric acid the fluorescence was green. [Found : C, 64·3 ; H, 5·5 ; $C_{14}H_{14}O_5$ requires C, 64·1; H, 5·3%.] Yield 1·5 g.

*7-Methoxy-8-methyl-coumarin-3-carboxylic acid* (*VIII*).—The above ester (1 g.) was treated with excess of alcoholic potash (20 c.c. of alcohol containing 3 g. of potassium hydroxide) and allowed to stand for 3 days. The clear solution was then diluted with water and acidified with dilute hydrochloric acid. The precipitated solid was filtered and purified by dissolution in aqueous sodium carbonate and reprecipitation. When finally crystallised from alcohol it came out as light yellow needles and rectangular plates melting at 211–212°. It resembled the ester very closely in the nature of its fluorescence. [Found: C, 61·4; H, 4·6; $C_{12}H_{10}O_5$ requires C, 61·6; H, 4·3%.]

*7-Methoxy-8-methyl-coumarin* (*IX*).—The above carboxylic acid (0·5 g.) was heated with quinoline (20 c.c.) and copper bronze ( 1 g.) for ¾ hour at 150–60° in an oil-bath. After cooling, the mixture was treated with excess of ether and the solution quickly filtered. Ether was then distilled off; the residue was treated with excess of dilute hydrochloric acid and the mixture was repeatedly shaken with ether. The ether extract was washed free from acid with aqueous sodium bicarbonate and then water and finally evaporated. The resulting solid was extracted with petroleum ether, whereby some resin was left behind. The petroleum extract was evaporated and the solid residue crystallised from alcohol. Colourless rectangular prisms and plates were thus obtained melting at 122–23°. The substance gave a weak violet fluorescence in alcohol and a bluish green fluorescence in concentrated sulphuric acid. It was found to be identical with the sample of 7-methoxy-8-methyl-coumarin prepared from 2-methyl-resorcinol as given below. [Found: C, 69·7; H, 5·5; $C_{11}H_{10}O_3$ requires C, 69·5; H, 5·3%.]

*7-Hydroxy-8-methyl-coumarin* (*X*): *Method I.*—An intimate mixture of 2-methyl-resorcinol (1 g., 1 mol.), malic acid (1·2 g., 1 mol.), and concentrated sulphuric acid (2·5 c.c.) was heated in an oil-bath maintained at 120° until effervescence ceased (1½ hours). After cooling, the product was poured with stirring into excess of crushed ice and left overnight. The solid was then filtered and extracted with ether. By this treatment, a small quantity of insoluble resin was removed. After distilling off the solvent the residue was recrystallised from alcohol, when colourless triangular prisms melting at 231–232° were obtained. The substance gave a pale blue fluorescence in neutral alcoholic solution and it was bright bluish in alkaline solution. In concentrated sulphuric acid the colour of the fluorescence was bluish green. [Found: C, 72·6; H, 4·4 ; $C_{10}H_8O_3$ requires C, 72·7 ; H, 4·6%.]

*Method II* : *Reduction of 7-hydroxy-coumarin-8-aldehyde* (*XI*).—A solution of the aldehyde in glacial acetic acid was treated with palladium charcoal and shaken in an atmosphere of hydrogen till two molecular proportions of the gas were absorbed. The solution was then filtered and the solvent removed as far as possible by distillation under reduced pressure. The residue was then treated with water, the acetic acid remaining behind was neutralised with sodium carbonate and the mixture repeatedly extracted with ether. The ether solution was then shaken with saturated sodium bisulphite to remove any unreduced aldehyde and subsequently washed with water. After distilling off the solvent the residue was recrystallised from alcohol whereby 8-methyl-7-hydroxy coumarin was obtained melting at 231–32°. A mixture of this specimen with the one made from 2-methyl-resorcinol melted at the same temperature. [Found: C, 72·5; H, 4·5; $C_{10}H_8O_3$ requires C, 72·7; H, 4·6%.]

7-*Methoxy*-8-*methyl-coumarin* (*IX*).—The above hydroxy coumarin (1 g.) was dissolved in anhydrous acetone (20 c.c.), excess of methyl iodide (2 c.c.) and potassium carbonate (2 g.) added and the mixture gently boiled under reflux for 20 hours. After filtering, the clear solution was distilled in order to recover the solvent, the solid residue was taken up in ether and washed with dilute sodium hydroxide in order to remove unmethylated hydroxy compound. After final washing with water, it was evaporated and the residue crystallised from alcohol. Colourless rectangular prisms and plates melting at 122–23° were obtained. This sample was found to be identical with the one prepared from the nuclear methylation product of β-resorcylic aldehyde. [Found: C, 69·4; H, 5·6; $C_{11}H_{10}O_3$ requires C, 69·5; H, 5·3%.]

*Summary*

A survey of past work on the nuclear methylation and ethylation of resorcinol and phloroglucinol derivatives is given and a mechanism for this reaction suggested. The nuclear methylation of β-resorcylic aldehyde has now been carried out giving rise to a good yield of the product (A). Its constitution as 4-methoxy-3-methyl-2-hydroxy benzaldehyde has been established in two ways: (i) A sample of 4-methoxy-3-methyl-2-hydroxy benzaldehyde was prepared according to the synthetic method of Jones and Robertson and compared with (A). (ii) The corresponding coumarin was prepared from (A) and was identified as 7-methoxy-8-methyl coumarin by comparison with the compound obtained by independent synthesis, starting from 2-methyl-resorcinol and passing through 7-hydroxy-8-methyl-coumarin as an intermediate stage. The same coumarin was also prepared by the reduction of umbelliferone-8-aldehyde and subsequent methylation.

## REFERENCES


1. Robinson and Shah .. *J. C. S.*, 1934, 1491.
2. Shah and Samant .. *Proc. Ind. Acad. Sci.* (A), 1938, **7**, 266–68.
3. Perkin .. *J. C. S.*, 1895, 990.
4. Herzig and Wenzel .. *Montash.*, 1903, **24**, 906.
5. Jones and Robertson .. *J. C. S.*, 1932, 1689.
6. Kauffler .. *Montash.*, 1800, **21**, 993.
7. Greger .. *Ibid.*, 1894, **15**, 437.
8. Wechler .. *Ibid.*, 1894, **15**, 239.
9. Crabtree and Robinson .. *J. C. S.*, 1918, **113**, 868.
10. Rangaswami and Seshadri *Proc. Ind. Acad. Sci.* (A), 8, 1938, 214–19.
11. Hems and Todd .. *J. C. S.*, 1940, 1208.
12. Tiemann and Parrisius .. *Ber.*, 1880, **13**, 2366.
13. Claisen and Eisleb .. *Ann.*, 1913, **401**, 21–119.
14. OTT and Nauen .. *Ber.*, 1922, **55B**, 920–29.
15. Goulding and Pelly .. *Chemical Abstracts*, **2**, 1708.
16. Srinivasa Rao and Sesha Iyengar .. " Perfumery, *Essent. Oil Record*," 1923, **14**, 300–01.
17. Solacoln, Mavrodin and Hermann .. *J. Phar. Chim.*, 1935, **22**, 548–56.
18. Dutt, Ghosh and Chopra .. *Arch. Phar.*, 1938, **276**, 333–40.
19. Spaeth and Pailer .. *Ber.*, 1935, 941.
20. Michael .. *Ibid.*, 1905, **38**, 3217.
21. Claisen and Haase .. *Ibid.*, 1900, **33**, 1242, 3778.

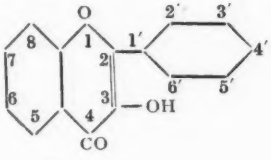
# THE CONSTITUTIONAL FEATURES OF ANTHOXANTHINS IN RELATION TO THE MORIN REACTION IN ANALYTICAL CHEMISTRY

## Part I. Some Naturally Occurring Hydroxy-flavonols and Flavanones

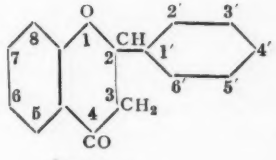
By K. Neelakantam and L. Ramachandra Row
*(From the Department of Chemistry, Andhra University, Waltair)*

Received August 5, 1941

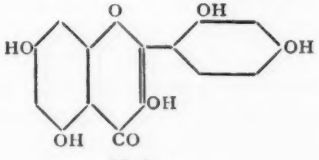
Morin (5 : 7 : 2′ : 4′-tetrahydroxyflavonol) was first introduced by Goppelsroeder[1] in 1868 as a reagent for the detection of small amounts of aluminium with which it yields in weakly acid solutions, a very prominent green or blue-green fluorescence ordinarily visible in daylight. This reaction did not receive much attention until Schantl[2] in 1924 showed that it is a very sensitive reaction, as little as $10^{-8}$ mg. of the element in 10 c.c. of the solution being detected with the aid of Tswett's luminoscope. Since then it has received considerable attention, as a result of which it is now known not to be specific for aluminium. A similar yellowish green fluorescence has also been obtained with beryllium,[2] and a large number of other metals, and the acid radicals, arsenite and arsenate.[3, 4, 5] In spite of this defect, this reaction has been utilised for the detection, as well as determination of aluminium and beryllium, and the fluoride ion indirectly.[3, 6, 9] However, no attempt has been made till now to study the influence of constitutional factors in morin over the appearance of fluorescence with aluminium or any of the other metals.




Flavonol




Flavanone




Morin

The correlation of constitution with fluorescence is a problem of considerable difficulty. In the group of hydroxyflavonols of which morin is one, a considerable amount of investigation has been done regarding the relation between number and position of hydroxyls and the tinctorial properties of these compounds,[10] but not much work has yet been done regarding the fluorescence which some of them exhibit under certain conditions. It is only recently that Rangaswami and Seshadri[11] examined this problem with reference to the closely allied hydroxy-flavones.

Several of the naturally occurring as well as the synthetic flavonols exhibit fluorescence in daylight, when dissolved in concentrated sulphuric acid, and a few in alkaline solution. Fisetin and the isomeric 6: 3′: 4′-trihydroxy-flavonol are exceptional in that they exhibit fluorescence in alcoholic solutions. Morin itself yields a bluish green fluorescence in concentrated sulphuric acid, but none in alkaline solutions. It is, however, a unique case of a hydroxy-flavonol which yields fluorescence with metals in alkaline or acid solutions and so far employed in analytical chemistry. As is well known, the hydroxy-flavonols have marked dyeing properties and yield coloured lakes with metals such as aluminium, beryllium, etc. Morin behaves similarly but surprisingly enough it yields with the same metals in dilute solutions very prominent fluorescence in daylight itslef. This fluorescence has been ascribed to a neutral, colloidally dispersed aluminium salt of morin having the formula $Al(C_{15}H_9O_7)_3$[2] but it seems probable that the paraquinonoid structure which these lakes possess[10] also plays an important part. The fact that a wide variety of metals yields similar fluorescence seems to support this view.

As a result of the investigations on the anthoxanthin pigments of flowers which have been in progress in these laboratories for several years, a number of compounds which have certain similarities and certain differences when compared with morin were available and, therefore, it was considered desirable to examine them in order to throw more light on the problem of the fluorescence obtained in the morin reactions. The examination was, however, limited to the reaction of morin with aluminium and beryllium as in practice this reaction is mostly used for the detection and determination of these metals.

## *Experimental*

For the following experiments pure samples of the flavanones, naringenin, butin and hesperitin, and the flavonols, kæmpferol, quercetin, herbacetin, gossypetin and quercetagetin which were obtained from natural sources were used.

*Preparation of Solutions*

*Reagents.*—Saturated solutions of all the pigments, except kæmpferol and herbacetin, in methyl alcohol were employed. The available amount of kæmpferol and herbacetin being small only dilute solutions were used.

*Test Solutions*: (1) *Aluminium.*—A dilute solution of potash alum was prepared using A.R. quality sample and standardised by precipitating the aluminium with 8-oxyquinoline. It was then diluted to contain 1 mg. of aluminium per c.c.

(2) *Beryllium.*—A dilute solution of beryllium nitrate was prepared using a "Pure" sample and the absence of aluminium was assured by testing with "Oxine". It was standardised by precipitating the beryllium as hydroxide and igniting to the oxide, and then diluted to contain 1 mg. of beryllium per c.c.

(3) *Potash.*—A dilute (2 N) solution of potassium hydroxide was prepared and tested for the absence of aluminium by the "Oxine" method.

*Procedure.*—Tests were carried out in alkaline, as well as in solutions acidified with acetic acid, with aluminium and beryllium provided the reagent itself did not undergo atmospheric oxidation in alkaline solution.

One c.c. of the test solution was placed in a quartz test-tube and treated with dilute potash until precipitation occurred. Thereafter, the precipitate was either dissolved in acetic acid or in an excess of the alkali, the solution diluted to 10 c.c. with water and treated with one or more drops of the reagent. Observations were made first in daylight and then under the "Cenco Black Light Source" which consists of an argon-mixed gas glow lamp provided with a U.V. filter which allowed light down to 3100 Å to pass through.

*Results*

Blank tests were carried out in all cases on the reagents themselves under identical conditions; the results were negative in all except hesperitin, 4′-methoxy-3′: 5: 7-trihydroxyflavanone (*Citrus aurantium* peels) which gave in alkaline solution under the lamp a bright blue fluorescence which was destroyed by acetic acid. Similar results were obtained with hesperitin in alkaline as well as in acetic acid solutions both with aluminium and beryllium. For comparison the reactions were carried out with a saturated solution of morin in methyl alcohol. With the reagents recorded in the table below, however, no fluorescence was observed in daylight and in no case was it so very prominent as with morin under identical conditions. The results obtained under the lamp are recorded in a tabular form below:

| Reagent | Sources | Aluminium | Beryllium | Remarks |
|---|---|---|---|---|
| 1. Naringenin. (5:7:4′-trihydroxy-flavanone). | Flowers of *Citrus decumana*. | Faint bluish fluorescence in acetic acid; alkaline solution yellow in colour but no fluorescence. | Faint bluish fluorescence in acetic acid; alkaline solution deep yellow with a bluish fluorescence. | |
| 2. Kæmpferol. (5:7:4′-trihydroxy-flavonol) | Senna leaves. | Alkaline solution yellow in colour with no fluorescence. In faintly alkaline or almost neutral solution, a bluish green fluorescence, moderately strong; on adding acetic acid the fluorescence is practically unchanged. | Bright yellow solution in alkalies with a bright greenish yellow fluorescence. None in acetic acid. | |
| 3. Herbacetin. (5:7:8:4-tetrahydroxy flavonol) | Flowers of *Gossypium herbaceum*. | Bright yellow solution with no fluorescence in acetic acid. | Bright yellow solution, with no fluorescence in acetic acid. | The reagent undergoes oxidation in alkaline solutions. |
| 4. Morin. (5:7:2′:4′-tetrahydroxy-flavonol) | Schering–Kahlbaum, Berlin. | In acetic acid extraordinarily brilliant green fluorescence; in alkaline solutions deep yellow without any fluorescence. | In acetic acid no fluorescence; in alkaline solution chromate yellow with deep yellowish green fluorescence. | Identical results were obtained even in daylight in both cases. |
| 5. Quercetin. (5:7:3′:4′-tetrahydroxy-flavonol) | Flowers of *Gossypium herbaceum* | Bright yellow solution with yellowish green fluorescence in acetic acid; deep yellow solution with no fluorescence in alkalies. | Bright yellow solution with no fluorescence in acetic acid; deep yellow solution with a very feeble greenish fluorescence in alkalies. | |
| 6. Gossypetin. (5:7:8:3′:4′-pentahydroxy-flavonol) | Do. | Yellow solution with no fluorescence in acetic acid. | Pale yellow solution with no fluorescence in acetic acid. | Undergoes oxidation in alkaline solutions. |
| 7. Quercetagetin. (5:6:7:3:4′-pentahydroxy-flavonol) | Flowers of *Tagetus erecta*. | Yellow solution with no fluorescence in acetic acid. | Yellow solution without any fluorescence in acetic acid. | Undergoes oxidation in alkaline solutions. |
| 8. Butin. (7:3′:4′-trihydroxy-flavanone). | Flowers of *Butea frondosa*. | In acetic acid solution pale yellow with no fluorescence; in alkaline solution, only red with no fluorescence. | In acetic acid pale yellow solution with no fluorescence; in alkalies a red solution with no fluorescence. | In alkaline solution the compound is converted rapidly into the corresponding chalkone, butein. |

*Discussion*

The results obtained show that among the group of compounds examined morin is exceptional in giving a very prominent fluorescence; none of the others gives any fluorescence with aluminium or beryllium in daylight and the fluorescence observed under the lamp is not at all so intense. A comparison of these results, however, throws light on the relation between the constitution of these compounds and the fluorescence. The only difference between morin and quercetin is in the 2′- instead of 3′- position of one hydroxyl in the side phenyl group and the difference in behaviour may, therefore, be due to the 2′-position of one hydroxyl. The results obtained with kæmpferol and morin show the intensifying effect of a hydroxyl in the 2′-position on the fluorescence given by a 4′-hydroxy compound. A comparison of kæmpferol with herbacetin reveals the inhibitory effect of the 8-hydroxyl. This conclusion is further supported by the comparison of quercetin with gossypetin. Further the available data shows the inhibitory effect of 6-hydroxyl as in quercetagetin. The exhibition of fluorescence both by kæmpferol and naringenin shows that the 3-hydroxyl is not absolutely necessary for the appearance of fluorescence with metals. It thus appears probable that a hydroxyl in 2′-position alone or in conjunction with a 4′-hydroxyl is responsible for the brilliant fluorescence obtained with morin and metals. This conclusion seems to be supported by the fact that morin unlike other flavonols, yields an anhydrosulphate ($C_{15}H_8O_6$, $H_2SO_4$) when treated with concentrated sulphuric acid, and this behaviour is closely related to the presence of a hydroxyl in the 2′-position.[12] If this conclusion were correct, similarly constituted compounds such as datiscetin (5 : 7 : 2′-trihydroxyflavonol), resomorin (7 : 2′ : 4′-trihydroxyflavonol), and 5 : 7 : 2′ : 4′-tetrahydroxyflavone synthesised by Robinson and Venkata Raman,[12] should yield similar results with metals. Further work is in progress along these lines.

The authors wish to thank Prof. T. R. Seshadri for help and encouragement during the course of this investigation.

## REFERENCES


1. Goppelsroeder .. *J. Prakt. Chem.*, 1867, **101**, 408; *Z. Anal. Chem.*, 1868, **7**, 195.
2. Schantl .. *Mikrochemie*, 1924, **2**, 174; *cf. Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 430.
3. Beck .. *Mikrochim. Acta*, 1937, **2**, 287; *Cf. Chem. Abs.*, 1938, 1606.
4. Sandell .. *Ind. Eng. Chem., Anal. Ed.*, 1940, **12**, 762.
5. Hidehiro Goto .. *Chem. Abs.*, 1941, 1720.
6. Zermatten .. *Ibid.*, 1934, 1957.
7. Sandell .. *Ind. Eng. Chem., Anal. Ed.*, 1940, **12**, 674.
8. Okâc .. *Chem. Abs.*, 1938, 5721.
9. White and Lowe .. *Ind. Eng. Chem., Anal. Ed.*, 1940, **12**, 229.
10. Thorpe .. *Dictionary of Applied Chemistry*, 1922, **3**, 220.
11. Rangaswami and Seshadri *Proc. Ind. Acad. Sci.*, 1940, **12**, 375.
12. Robinson and Venkata Raman *J. C. S.*, 1929, 61.

# A RELATION BETWEEN A PENCIL AND A RANGE OF QUADRICS*

By Sahib Ram Mandan

*(The University of the Panjab, Lahore)*

Received June 20, 1941

(Communicated by Prof. C. V. H. Rao)

The purpose of this paper is to establish a relation between a pencil and a range of quadrics and thence deduce the equivalence of two symmetrical determinants differing in order by unity.

1. *We start with the quadrics* $\Sigma$, $\Sigma_i$, $(i=1, 2)$ *of a pencil. Let* C, C′ *be the enveloping cones of* $\Sigma$ *and* $\Sigma_1$ *having their vertices at the poles* P, P′ *of a plane* $\Pi'$ *w.r.t.* $\Sigma$ *and* $\Sigma_1$ *respectively,* i.e., *the cones and the quadrics have the same plane of contact* $\Pi'$. *Now if* $\Sigma_2$ *pass through the twisted quartic common to* C *and* C′, P′ *will lie on the quadric* $\Sigma_1'$ *reciprocal of* $\Sigma$ *w.r.t. a quadric* $\Sigma_{12}$ *for which* $\Sigma_1$ *and* $\Sigma_2$ *are reciprocal. We thus arrive at the quadrics* $\Sigma'$, $\Sigma_i$ *of a range.*

As P, P′ are the vertices of two cones of the pencil of quadrics of which $\Sigma_2$ is a member, the polar plane $\Pi$ of P w.r.t. $\Sigma_2$ passes through P′ and is the polar plane of the line PP′ w.r.t. C′. The pole of $\Pi$ w.r.t. $\Sigma_1$ is therefore conjugate to P w.r.t. $\Sigma$ and in such a case it can be proved that $\Pi$ touches $\Sigma'$. Now the poles of a plane w.r.t. a range of quadrics lie on a line, the point of contact of $\Pi$ with $\Sigma'$ is therefore found to be P′, *i.e.*, P′ lies on $\Sigma'$.

2. Let the point-equations of $\Sigma_i$ be $S_i\,(x, y, z, t) \equiv a_i x^2 + \cdots + 2\,f_i\,yz + \cdots + 2\,u_i xt + \cdots = 0$ and their tangential equations be $\Sigma_i\,(l, m, n, p) \equiv A_i l^2 + \cdots + 2\,F_i mn + \cdots + 2\,U_i lt + \cdots = 0$ with usual notations for $A_i, \cdots, F_i, \cdots, V_i \cdots$

Consider the equation $Q \equiv \lambda S_2\,(x, y, z, t) + S_1\,(x, y, z, t) \cdot S_1 - \Pi'^2 = 0$ where $S_i$ stands for $S_i\,(\alpha, \beta, \gamma, \delta)$; $\Pi' \equiv xS_{1\alpha} + yS_{1\beta} + zS_{1\gamma} + tS_{1\delta}$; $2\,S_{1\alpha} \equiv \dfrac{\partial S_1}{\partial \alpha}$, $2\,S_{1\beta} \equiv \dfrac{\partial S_1}{\partial \beta}, \cdots S_1$, $\lambda \neq 0$. Now $S_1\,(x, y, z) \cdot S_1 - \Pi'^2 = 0$ represents an enveloping cone C′ of $\Sigma_1$ having its vertex at P′ $(\alpha, \beta, \gamma, \delta)$. Suppose the

* Read at the *Second Subject Conference in Mathematics of the Punjab University,* March 28, 1941.

quadric $Q=0$ to be a cone C, its discriminant then must vanish, *i.e.*, $\alpha$, $\beta$, $\gamma$, $\delta$ should satisfy the condition given by the equation $D_1'=0$ where

$$D_1' \equiv \begin{vmatrix} \lambda a_2+a_1S_1-S_{1\alpha}^2, & \lambda h_2+h_1S_1-S_{1\alpha}S_{1\beta}, & \lambda g_2+g_1S_1-S_{1\alpha}S_{1\gamma}, & \lambda u_2+u_1S_1-S_{1\alpha}S_{1\delta} \\ & \lambda b_2+b_1S_1-S_{1\beta}^2, & \lambda f_2+f_1S_1-S_{1\beta}S_{1\gamma}, & \lambda v_2+v_1S_1-S_{1\beta}S_{1\delta} \\ & & \lambda C_2+C_1S_1-S_{1\gamma}^2, & \lambda w_2+w_1S_1-S_{1\gamma}S_{1\delta} \\ & & & \lambda a_2+a_1S_1-S_{1\delta}^2 \end{vmatrix}$$

Again taking the quadric $\Sigma$ as $\lambda S_2(x, y, z, t)+S_1(x, y, z, t)\cdot S_1=0$ and the plane $\Pi'$ as $\Pi'=0$, we find that the cones C, C′ satisfy the conditions imposed upon them in §1. Therefore, P′ lies on the quadric $\Sigma'$ whose tangential equation will be $\lambda\cdot\dfrac{\Sigma_1(l, m, n, p)}{\Delta_1}+\dfrac{\Sigma_2(l, m, n, p)}{\Delta_2}\cdot S_1=0$ where $\Delta_i$ $(\neq 0)$ is the discriminant of the quadric $S_i(x, y, z, t)=0$, *i.e.*, $\alpha$, $\beta$, $\gamma$, $\delta$ should satisfy the equation $D_2'=0$ where

$$D_2' \equiv \begin{vmatrix} \dfrac{\lambda A_1}{\Delta_1}+\dfrac{A_2}{\Delta_2}S_1, & \dfrac{\lambda H_1}{\Delta_1}+\dfrac{H_2}{\Delta_2}S_1, & \dfrac{\lambda G_1}{\Delta_1}+\dfrac{G_2}{\Delta_2}S_1, & \dfrac{\lambda U_1}{\Delta_1}+\dfrac{U_2}{\Delta_2}S_1, & \alpha \\ & \dfrac{\lambda B_1}{\Delta_1}+\dfrac{B_2}{\Delta_2}S_1 & .. & .. & \beta \\ & & .. & .. & \gamma \\ & & & .. & \delta \\ & & & & 0 \end{vmatrix}$$

*The two determinantal equations* $D_i'=0$ *arise from the same proposition looked from two different angles. Hence they must be equivalent*, i.e., $D_1'\equiv KD_2'$. This equality can be otherwise* proved immediately and directly if $D_1'$ be written in the following form (ignoring a multiplicative constant).

$$\begin{vmatrix} \dfrac{\lambda a_2}{S_1}+a_1, & \ldots\ldots\ldots\ldots & S_{1\alpha} \\ & \dfrac{\lambda b_2}{S_1}+b_1, \ldots\ldots\ldots & S_{1\beta} \\ & & \ldots\ldots\ldots S_{1\gamma} \\ & & \ldots S_{1\delta} \\ S_{2\alpha}, & S_{2\beta}, \quad S_{2\gamma}, \quad S_{2\delta}, & 0 \end{vmatrix}$$

and writing $\lambda=\mu S_1$, it assumes a good symmetric form in both $S_1$ and $S_2$.

* Suggested by the referee.

3. Further, let $\Sigma_i$, be the quadrics as in §2 and consider the quadric $Q \equiv \lambda S_2(x, y, z, t) + C' = 0$ where $C' \equiv \psi_\alpha^2 S_1(x, y, z, t) + \psi_x(\psi_x S_1 - 2\psi_\alpha \Pi')$ $S_i$, $\Pi'$ being as in § 2, $\psi_x \equiv ax + by + cz + dt$, $\psi_2 \equiv a\alpha + b\beta + c\gamma + d\delta$ $(\neq 0)$. Now if we call the conic $S_1(x, y, z, t) = 0 = \psi_x$ as $\sigma_1$, $C' = 0$ will represent the cone $C'$ passing through $\sigma_1$ with its vertex at $P'(\alpha, \beta, \gamma, \delta)$. Suppose the quadric Q to be a cone, then its discriminant must vanish, *i.e.*, $\alpha, \beta, \gamma, \delta$ should satisfy the condition expressed by the equation $D_1' = 0$ where $D_1' \equiv$

$$\begin{vmatrix} \lambda a_2 + \psi_\alpha^2 a_1 + a^2 S_1 & \lambda h_2 + \psi_\alpha^2 h_1 + ab S_1 & \lambda g_2 + \psi_2^2 g_1 + ca S_1 & \lambda u_2 + \psi_2^2 u_1 + ad S_1 \\ -2a\psi_\alpha S_{1\alpha}, & -\psi_\alpha(aS_{1\beta} + bS_{1\alpha}), & -\psi_\alpha(cS_{1\alpha} + aS_{1\gamma}), & -\psi_\alpha(aS_{1\delta} + S_{1\alpha}) \\ & \lambda b_2 + \psi_\alpha^2 b_1 + b^2 S_1 & .. & .. \\ & -2b\psi_\alpha S_{1\beta}, & & \\ & & .. & .. \\ & & & .. \end{vmatrix}$$

Again let V (A, B, C, D) be the pole of the plane $\psi_x = 0$ w.r.t. $\Sigma_2$ and $S_i(V) \equiv S_i(A, B, C, D)$; $2S_{iA} = \frac{\partial S_i(V)}{\partial A}$, $\cdots$, $\cdots$, $\cdots$, $\psi_A = aA + bB + cC + dD$; $C_1' \equiv S_1(x, y, z, t) + \frac{\psi_x}{\psi_A^2}[\psi_x S_1(V) - 2\psi_A(xS_{1A} + \cdots + \cdots + \cdots)]$; $C_2' \equiv S_2(x, y, z, t) - \frac{\psi_x^2}{S_2(V)}$; $\Sigma_1' \equiv C_1' + \lambda \frac{\psi_x^2}{\psi_\alpha^2 S_2(V)}$, $\Sigma \equiv \lambda C_2' + \psi_\alpha^2 \Sigma_1'$, then $Q \equiv \Sigma + \psi_x \cdot \psi_{x'}$ where $\psi_{x'} \equiv \psi_x\left[(S_1 - S_1(V)\left(\frac{\psi_\alpha}{\psi_A}\right)^2\right]$ $- 2\psi_\alpha\left[xS_{1\alpha} + \cdots - \frac{\psi_\alpha}{\psi_A}(xS_{1A} + \cdots + \cdots)\right]$.

Let $\psi$, $\psi'$ be the planes $\psi_x = 0$ and $\psi_{x'} = 0$, $\mu$ be their common line; P be the vertex of the cone Q and $\Pi''$ be the polar plane of P w.r.t. the quadric $\Sigma = 0$. Now it is easy to see that the planes $P\mu$ and $V\mu$ are harmonically conjugate w.r.t. the planes $\psi$ and $\psi_{x'} + \frac{\lambda\psi_x}{S_2(V)} = 0$, and the planes $\psi$, $\psi'$ are separated harmonically by the pairs of planes $P'\mu$, $V\mu$; $\Pi''$, $P\mu$; $\psi_{x'} + \frac{\lambda\psi_x}{S_2(V)} = 0$, $\psi_{x'} - \frac{\lambda\psi_x}{S_2(V)} = 0$ as $Q \equiv \lambda C_2' + \psi_\alpha^2 C_1' + \psi_x\left(\psi_{x'} + \frac{\lambda\psi_x}{S_2(V)}\right)$ $\equiv \Sigma + \psi_x\psi_{x'}$ and $C' \equiv C_1'\psi_\alpha^2 + \psi_x\psi_{x'}$. From these results and that $C' \equiv \psi_\alpha^2 \Sigma_1' + \psi_x\left(\psi_{x'} - \frac{\lambda\psi_x}{S_2(V)}\right)$ it follows that the polar plane of P' w.r.t. the quadric $\Sigma_1' = 0$ is $\Pi''$ as the harmonic conjugate of the plane $P'\mu$ w.r.t. $\psi$ and $\psi_{x'} - \frac{\lambda\psi_x}{S_2(V)} = 0$.

Now the quadric $\Sigma_2$ and the cones Q, C′ belong to a pencil, therefore the polar plane $\Pi$ of P w.r.t. $\Sigma_2$ passes through P′ and is the polar plane of the line PP′ w.r.t. C′. The pole of the plane $\Pi$ w.r.t. $\Sigma_1' = 0$ is hence conjugate to P and in such a case it can be proved that $\Pi$ touches the quadric $\Sigma'$, reciprocal of $\Sigma = 0$ w.r.t. a quadric $\Sigma_{12}'$ for which $\Sigma_1' = 0$ and $\Sigma_2$ are reciprocal.

Again *the quadrics* $\Sigma = 0$, $\Sigma_1' = 0$ *and the cone* $C_2'$ *belong to a pencil,* $C_2'$, being the enveloping cone of $\Sigma_2$ with its vertex at V, reciprocates into the conic $\sigma_1$ w.r.t. $\Sigma'_{12}$; $\Sigma'$, $\Sigma_2$, $\sigma_1$ *therefore belong to a range.* The pole of the plane $\Pi$ w.r.t. $\sigma_1$ being the point where the line PP′ meets $\psi$, the point of its contact with $\Sigma'$ will be no other than the point P′. Hence P′ lies on $\Sigma'$ whose tangential equation will be

$$\frac{\lambda\,[\Sigma_1(l, m, n, p)\cdot\Sigma_1 - (l\Sigma_{1a} + m\Sigma_{1b} + \cdots + \cdots)^2]}{\Delta_1\cdot\Sigma_1} + \psi_\alpha{}^2\,\frac{\Sigma_2(l, m, n, p)}{\Delta_2} = 0$$

where $\Sigma_i \equiv \Sigma_i(a, b, c, d)\ (\neq 0)$; $2\,\Sigma_{ia} \equiv \dfrac{\partial\Sigma_i}{\partial a}$, $\cdots$, $\cdots$, $\cdots$, *i.e.*, $\alpha$, $\beta$, $\gamma$, $\delta$ should satisfy the condition expressed by the equation $D_2' = 0$ where $D_2' \equiv$

$$\begin{vmatrix} \dfrac{\lambda}{\Delta_1\Sigma_1}(A_1\Sigma_1 - \Sigma_{1a}{}^2) + \psi_\alpha{}^2\dfrac{A_2}{\Delta_2}, & \dfrac{\lambda}{\Delta_1\Sigma_1}(H_1\Sigma_1 - \Sigma_{1a}\Sigma_{1b}) + \psi_\alpha{}^2\dfrac{H_2}{\Delta_2}, & \dfrac{\lambda}{\Delta_1\Sigma_1}(G_1\Sigma_1 - \Sigma_{1a}\Sigma_{1c}) + \psi_\alpha{}^2\dfrac{G_2}{\Delta_2}, & \cdots; & \alpha \\ & \dfrac{\lambda}{\Delta_1\Sigma_1}(B_1\Sigma_1 - \Sigma_{1b}{}^2) + \psi_\alpha{}^2\dfrac{B_2}{\Delta_2} & \cdots, & \cdots; & \beta \\ & & \cdots, & \cdots; & \gamma \\ & & \cdots, & \cdots; & \delta \\ & & & & 0 \end{vmatrix}$$

*The two determinantal equations* $D_i' = 0$ *arise from the same proposition looked from two different points of view. Hence they must be equivalent,* i.e., $D_1' = KD_2'$*.

4. It may be remarked here that *if the quadric* Q *of* §3 *break into a pair of planes,* $\Sigma = 0$ *must degenerate into a cone with its vertex on the line* $\mu$ *and thence* $\Sigma'$ *degenerates into a conic.* From this result and the preceding one we can derive *certain properties of the focal conics of a confocal system by taking* $\sigma_1$ *as the circle at infinity.*

The work for this paper was carried through with the help of a research scholarship from the University of the Punjab.

* A similar analysis can be applied for this equality also to prove it directly and immediately as in §2.

954-41—Printed at The Bangalore Press, Bangalore City, by G. Srinivasa Rao, Superintendent and Published by The Indian Academy of Sciences, Bangalore

## ERRATA

*Vol.* XIV, *No.* 2, *August* 1941

P. 97, para 2, line 6 and p. 98, para 4, line 15 *read* $[\alpha]_D^{28}$ in chloroform $+26{\cdot}8°$ and that recorded for lupeol in the literature $+26{\cdot}4°$, for $41{\cdot}0$ and $41{\cdot}1$ respectively.